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ALLOYS OF IRON AND CHROMIUM

By V. N. Krivobok

Abstract

All metallic alloys, i.e., their physical characteristics are governed by the principles of physical chemistry.

Unless observed experimental results are explainable by these principles incorporated in the diagrams of the alloys, our knowledge and understanding is incomplete.

Iron-chromium systems may serve as an illustration and was chosen for that purpose. It was found that these alloys, practically free from carbon and other usual impurities including gases, are susceptible to age hardening. The same alloys show profound and rather sudden change in mechanical properties at certain chromium concentrations. They are subjected to volume changes at elevated temperatures. Hence they can not be of ideal solid solution type. And, it is thus quite conceivable that many industrial problems would find an answer only through further basic research.

This research, however, would have to deal with very complex questions since mere alterations in the diagrams of the alloys would not explain such observations as, for example, the influence of low and slightly elevated temperatures fully covered in the lecture, on certain mechanical properties of iron-chromium and iron-chromium-carbon alloys. Further,—as if the problem were not sufficiently difficult, the great affinity of chromium (and consequently chromium alloys) for nitrogen gas is carefully studied. Nitrogen, when present, acts much in the same manner as carbon, conferring upon alloys the ability to harden and generally alter their physical properties.

This is the Ninth Edward De Mille Campbell Memorial Lecture, presented by Dr. V. N. Krivobok, professor of metallurgy, Carnegie Institute of Technology, Pittsburgh, and associate director of research, Allegheny Steel Co., Brackenridge, Pa. The lecture was presented at the Sixteenth Annual Convention of the Society in New York City, October 3, 1934.

A FASCINATING pastime,—doubtless enjoyed by some of you, —is to turn backward and trace, through manuscripts centuries old, legends, and even songs, the first conceptions of that particular art, industry, or science to which we devote our labors. Gratifying as it is to observe the strides made through centuries, it is even more fascinating to follow the evolution of an art into a science.

There is a strange entrancement in the following quotation, which is attributed to Cardanus, naturalist, philosopher, and mathematician, who lived in the fifteenth century:

> "Steel is nobler than iron and exists in two forms; namely, as made steel and as native steel. When it is well cleaned, then heated, and quenched three or four times in equal parts of radishes and water which had contained earthworms, it cuts iron like lead."

The picturesque phraseology assists in resurrecting a picture of the status of metallurgy in that and preceding centuries: quaint and mysterious recipes, jealously guarded secrets of the metallurgical art.

A few hundreds of intervening years: Metallurgical industry rapidly becomes a potent factor in technological progress. Progress demands understanding. Through the accomplishments of Edward De Mille Campbell, Albert Sauveur, Henry Marion Howe, Sir William Roberts-Austen, Floris Osmond, Gustav Tammann, Dimitri Tchernoff, and many of their predecessors and contemporaries,—metallurgy and metallography take their legitimate place among other, older sciences. The brilliant researches of those distinguished scientists,—a sequence of logical thought,—served to establish fundamental principles by which could be explained not one, but many, seemingly unrelated, experimental facts, whether from the laboratory or from the works. Throughout all of the scientific researches of Professor Campbell is seen the influence of this attitude, so clearly expressed by Floris Osmond:

> "Modern science must treat metal like a living organism. We are led to study its anatomy, i.e., its physical and chemical constitution; its biology, i.e., the influence exerted upon its constitution by the various treatments, thermal and mechanical; and its pathology, i.e., the action of impurities and defective treatments upon its normal constitution."

You, who followed the leaders, have travelled far in your chosen field of endeavor. In many instances the course of modern research

was so laid out as to follow the expressed advice of Osmond. As a consequence, the understanding of fundamental facts in certain fields is well advanced. In others, however, such as the multiple complex alloys of iron, we merely accumulated vast amounts of experimental data, mostly pertaining to various properties. This accumulation is, no doubt, important; yet the fact should be faced that attempts at generalization are, at times, unsuccessful. Data emanating from various sources are frequently disconnected, in many instances contradictory, and, in some cases, quite mysterious. In the absence or in the incomplete understanding of fundamental premises it is an impossible task to eliminate the doubtful and preserve the reliable. One wonders if the study of metal "anatomy", as defined above, has not been neglected, unwillingly, of course, but still unwisely.

The profitable field of endeavor should be found in further inquiries into the anatomy of metals; not with the idea of merely securing abstract information, but for the purpose of analyzing and correlating it with existing and future biological and pathological knowledge. It should further be emphasized that such analysis should be careful and unbiased; those facts that may not fit into the structure of a certain branch of our knowledge as accepted today should not be shelved or disregarded without additional inquiries. Metallurgy has, as yet, only a few axioms.

The topic selected for this Campbell Memorial Lecture has been extensively studied. It is closely related, through underlying fundamental facts, to many other fields. The generally accepted theoretical concepts and independently secured experimental results are, in some cases, in obvious and perturbing disagreement. Finally, this particular field is very important from the humanitarian, engineering and artistic point of view.

These are the reasons why I have chosen, with, I feel, the silent approval of Edward De Mille Campbell, to offer a discussion of "Alloys of Iron and Chromium", a subject so illustrative of my belief in the wisdom of correlated studies of fundamental principles and their application to industrial problems.

The Nature of Iron-Chromium Alloys—Their Diagram

A broad statement (but basically true) may be made that in alloys the properties of the predominating metal are generally preserved, at least within some limits of composition. The introductory remarks alluded to the existence of some peculiar, as yet unexplained,

properties in alloys of iron and various elements, such as silicon, aluminum, chromium, and others. Before offering the discussion of iron alloys, it may be well to note that iron in itself is a somewhat unusual metal. It is, of course, general knowledge, that iron exists in two polymorphic modifications,[1] alpha, maintaining its identity up to 906 degrees Cent. (1663 degrees Fahr.),[2] gamma from 906 to 1401 degrees Cent. (1663-2555 degrees Fahr.) and then alpha (generally known as delta) again up to the melting point: the temperatures of 906 and 1401 degrees Cent. (1663-2555 degrees Fahr.) corresponding, as we all know, to A_3 and A_4 transformation points.

The identity of alpha and delta phases is universally accepted —at least, I have not received any dissenting statement from those of whom I have inquired. Accordingly, we encounter in iron the existence of one and the same polymorphic form, over different ranges of temperature, with these temperature ranges rather widely separated. To the best of our knowledge iron and cobalt are the only two metallic elements exhibiting such unique properties.[3]

It will be found that in alloys of iron and limited amounts of such elements as chromium, silicon, molybdenum, and others (existing as a series of solid solutions), the polymorphic history of iron is repeated. Should we wonder, then, if many iron alloys are much more complex than we anticipated? The polymorphic transformations, above referred to, take place in the same order, alpha to gamma and back to alpha, with the only difference that these transformations occur in solid solutions of variable composition instead of in pure metal. The temperatures of transformations are variously modified depending on the alloying element. In the system iron-chromium (Fig. 1) the alpha to gamma (A_3) point is first slightly lowered, then shifted upwards while the subsequent gamma to alpha (A_4) point is continuously lowered.

At a certain concentration,[4] different for different alloying elements, the two temperatures coincide, and, therefore, no polymorphic

[1]The "beta" iron may be conveniently excluded from our discussion.

[2]According to the latest work of Austin and Pierce (1) on high purity iron, the alpha to gamma transformation occurs at 928 degrees Cent. (1700 degrees Fahr.).

The figures appearing in parentheses refer to the bibliography appended to this lecture.

[3]Granted, however, that it is unusual, it is not contrary to the principles of thermodynamics. Without going into details, it may simply be stated that gamma iron has the smaller free energy between the A_3 and A_4 points; hence the spontaneous change in the direction from alpha to gamma. Upon further heating, the temperature coefficient of free energy of gamma iron exceeds that of alpha and above the A_4 point the reversed process, change from gamma iron to alpha, takes place. For the detailed study see book by Schenck, "*Physicalische und Chemische Eisenhüttenprozesse*, or a pamphlet by Svetchnikoff on polymorphic transformations in metals (in Russian) *Journal of Technical Physics*, 1934, No. 2, p. 254, also Dehlinger, *Zeit. für Physik*, Vol. 65, 1931, p. 535.

transformation will occur: Beyond this particular concentration, solid alloys exist as one and the same[5] phase at all temperatures. The phase diagrams for such alloys are characterized by the presence of the so-called "gamma loop." Theoretically, one phase alloys (defining "phase" as a crystal structure) should be simple: Most of them belong, because of their atomic configuration and distribution, to the class of primary substitutional solid solution (in which solute atoms replace solvent atoms, the two kinds of atoms generally being distributed at random, and the lattice of the parent metal being retained).[6]

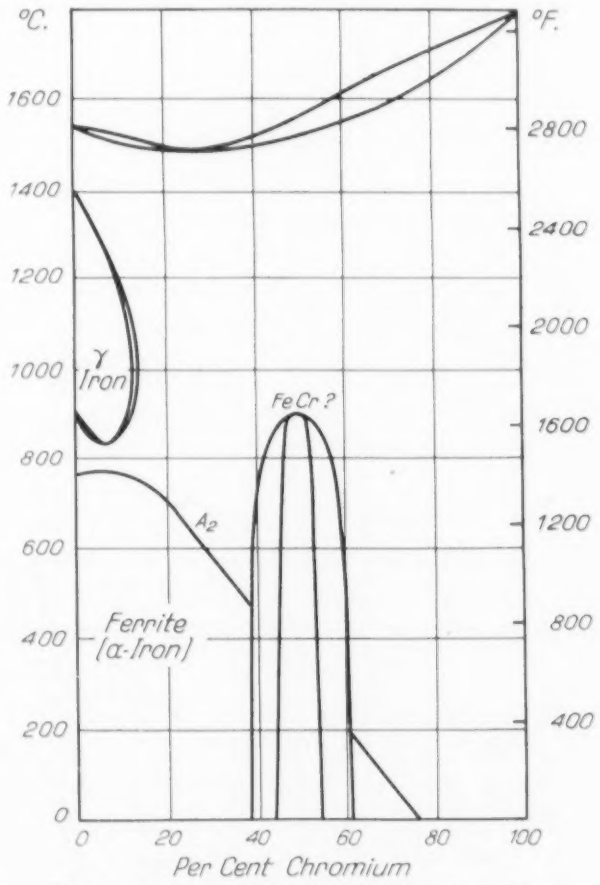

Fig. 1—Phase Diagram for Iron-chromium Alloys.

[4]See the work of Kinzel (37), Maurer (38), Kreutzer (7), Oberhoffer and Esser (5), and Vegesack (8).

[5]Except for lattice parameter, and excluding magnetic transformation (Curie point).

[6]Solid solutions are classified as follows:

1. (a) Primary substitutional, (b) Primary interstitial,
2. Secondary solid solutions, and
3. Intermetallic compounds of fixed or variable composition.

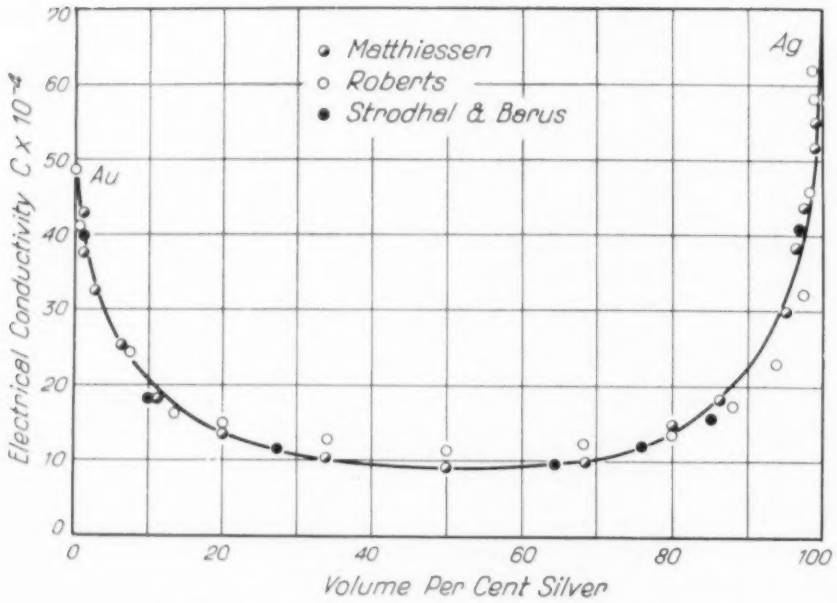

Fig. 2—Electrical Conductivity of Gold-silver Alloys.

The same characteristics are found in those alloys that form solid solutions over only a *limited* range of concentration: Copper-zinc, iron-manganese,—to name a few at random. The iron-chromium system may also be included—it is generally accepted that these two elements bond together in the manner of primary substitutional solutions. Since alloys of this class do not exhibit polymorphic transformation, their constitution upon heat treatment remains unchanged and their properties cannot be radically altered: Alloys preserve to a greater or lesser degree the individual characteristics of the predominating metal. Perhaps the most outstanding characteristic of the series of such alloys is that a change in concentration of the solute brings about a continuous change in properties. Many examples, some of which could truly be called classic, can be cited, especially in the nonferrous field. Almost any property (for example electric conductivity) could be selected to illustrate the general type of curve (Fig. 2) obtainable either in gold-silver or copper-nickel alloys, typical from among the primary substitutional groups. This behavior is not restricted to two-component systems: It is also found in the more complex multi-component alloys.

Three-Component System—Fe, Cr, C.

In most alloys of iron, carbon is usually present in appreciable

amounts: Carbon should, therefore, be considered as a third component. Ordinarily, even small amounts of carbon result in the formation of a new phase (carbide), but, in certain cases, it becomes

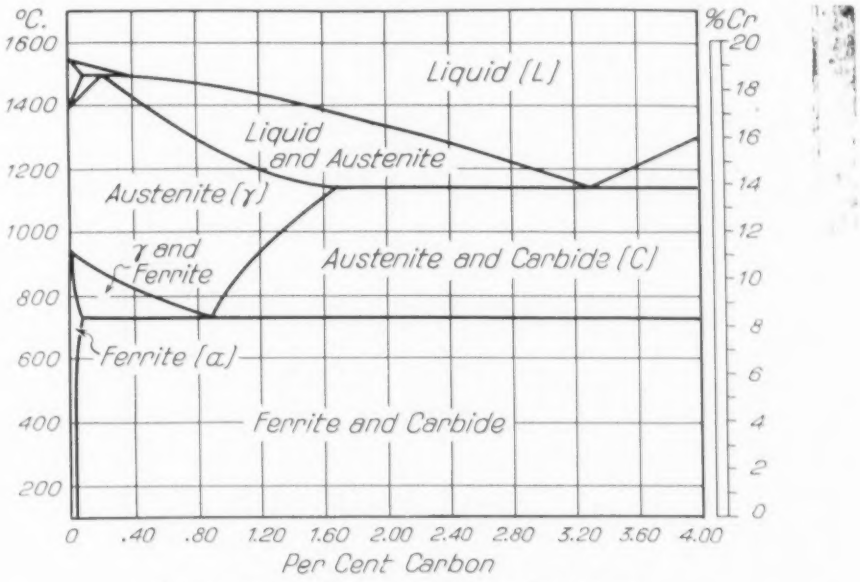

Fig. 3—Phase Diagram for Iron-carbon Alloys.

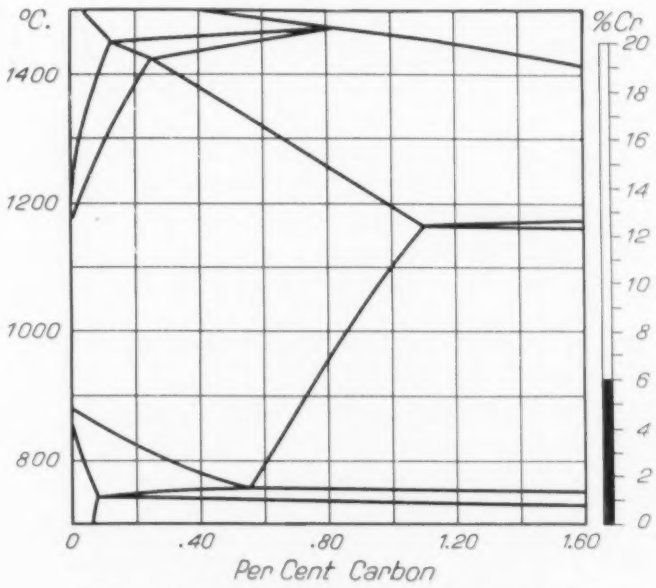

Fig. 4—Cross Section of the Phase Diagram for Iron-chromium-carbon Alloys Taken at 6 Per Cent Chromium.

an invisible and indistinguishable part of a solid solution. This is true, within limited concentrations, of iron-chromium-carbon alloys, and an attempt will be made to show it graphically. Any graphic

representation of the three-component system—necessarily a space model—by means of a drawing is not easy to comprehend. There is a way of presenting the change brought about by additions of

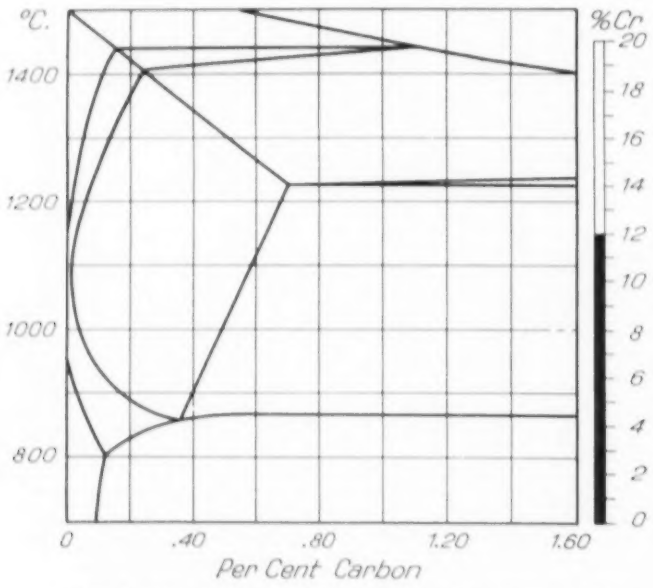

Fig. 5—Cross Section of the Phase Diagram for Iron-chromium-carbon Alloys Taken at 12 Per Cent Chromium.

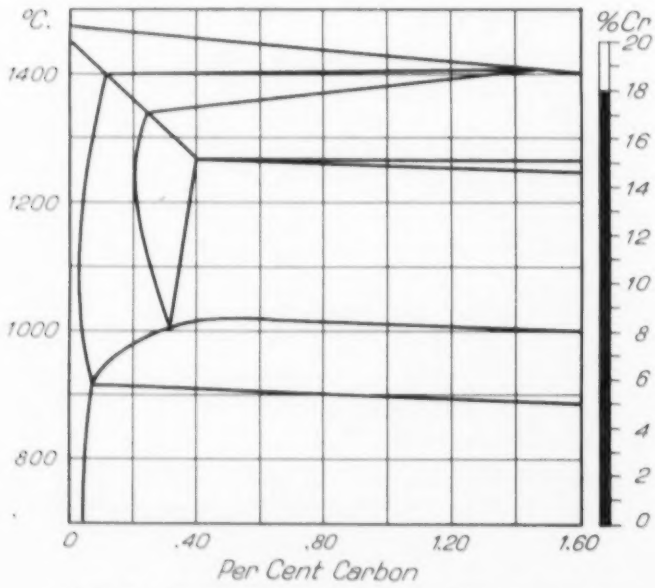

Fig. 6—Cross Section of the Phase Diagram for Iron-chromium-carbon Alloys Taken at 18 Per Cent Chromium.

chromium to the iron-carbon system through a series of cross-sectional diagrams, drawn parallel to the carbon concentration-

temperature plane: The film on the screen shows such cross sections at intervals of 2 per cent chromium. (Figs. 3 to 6).[7]

Briefly, the addition of chromium affects not only the composition of various phases and shifts the concentration of important points (such as eutectic or eutectoid), but, if the added percentage of chromium is sufficiently high, the phase relationship takes on a new aspect. The present discussion deals entirely with phenomena occurring in the solid state. It may, therefore, be advisable to concentrate on that part of the diagram with which we shall be primarily concerned, namely, the shifting and rearrangement of one-, two-, and three-phase (solid) regions. It is shown by means of animated drawings on the motion picture exhibited film.

It will be noted, as was already stated, that, beginning at a certain chromium concentration (Fig. 6), alloys containing appreciable amounts of carbon remain ferritic, i.e., constituted of one phase, alpha iron-chromium-carbon-solid solutions.[8] With increasing chromium concentration the one-phase region expands still further. Those alloys which lie within this field are similar in their nature,—to emphasize again,—to alloys without carbon. That is to say, they undergo no transformation with rising temperature, hence are not modified in their properties by heat treatment;[9] qualifying as to all requirements of solid solution, such alloys should also possess the typical properties of the latter.

Anomalies in Alloys of Solid-Solution Type

Quite contrary to our expectations, we find that the properties of various iron alloys exhibit pronounced deviations or even sharp discontinuities. In iron-silicon alloys, (15) of all others most carefully studied, the curve for lattice constants, mechanical strength, or in fact nearly every "property vs. concentration" curve, shows either a definite change in slope or beforementioned discontinuity. In iron-aluminum alloys, (25) the lattice parameter does not change as expected. In certain alloys of iron and nickel (26) we recognized unusual properties (such as thermal expansion), but lack a wholly satisfactory explanation. The epsilon phase[10] in iron-manganese

[7] In this paper the diagrams at 6 per cent chromium intervals are reproduced.

[8] In order to avoid unnecessary complexity, the separation of chromium-iron carbides, because of the changing solid solubility is, for the time being, neglected.

[9] This statement presupposes the alloys to be free of concentration gradients.

[10] Although iron-nickel and iron-manganese systems do not belong to the "gamma loop" class of alloys, their "peculiarities" are still pertinent to this discussion.

alloys (*27*) is still somewhat of a mystery. The diagrams for these alloys are not, as yet completed.

As we shall presently see, iron-chromium and iron-chromium-carbon alloys are no exception: experimental observations concerning their properties are not explained by their diagrams. These and other collisions of the expected and the observed caused many investigators to turn their attention to the fundamental study of solid solutions. Even though it is known that the properties of an alloy

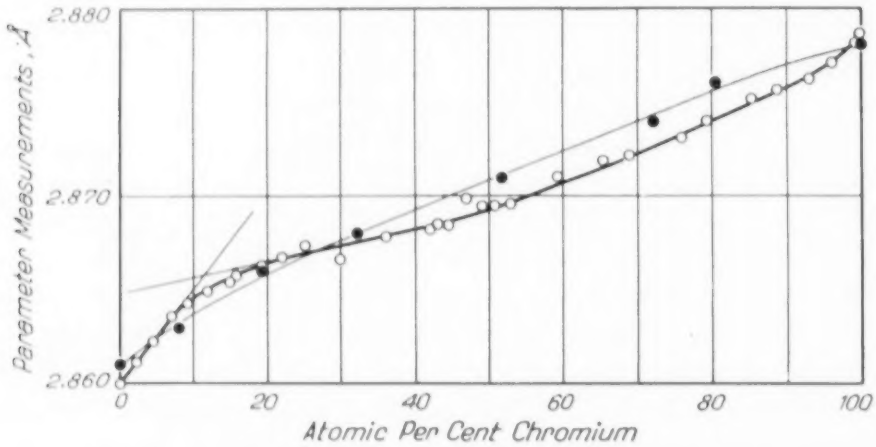

Fig. 7—Lattice Parameter for Iron-chromium Alloys. (After Adcock).

depend upon the properties of the constituent atoms and on the mutual effects of the dissimilar atoms, no way of anticipating deviations from the expected has been found, for it is now known that solid solutions exhibit all known violations of ideal-solution behavior. The alloys of iron and chromium are no exception.

The answers to these perplexing general questions cannot, as yet, be given: further, I hope that you do not expect them. After a brief review of the existing pertinent data for chromium alloys, recently secured observations and their brief discussion will be presented: If you should find in them leads for further scientific researches or for conquest over some of the industrial problems, I would like to think that the duty coincident with the honor of being Campbell Lecturer has been fulfilled.

Before submitting the results pertaining to anomalies found in iron-chromium alloys the basis for the assertion that these alloys are of solid solution type should be stated. This basis is found in the work of Oberhoffer and Esser (5), Kreutzer (7), (9), Westgren, Phragmen, and Negresco (6), Chevenard (10), and more recently,

of Preston (18), and Wever and Jellinghaus (17). The X-ray method was employed and type of lattice as well as its dimensions at room temperature were ascertained.

The results of Preston's work, which depicts the change in the parameter with composition is reproduced in Fig. 7.

This investigator comes to the conclusion that iron and chromium

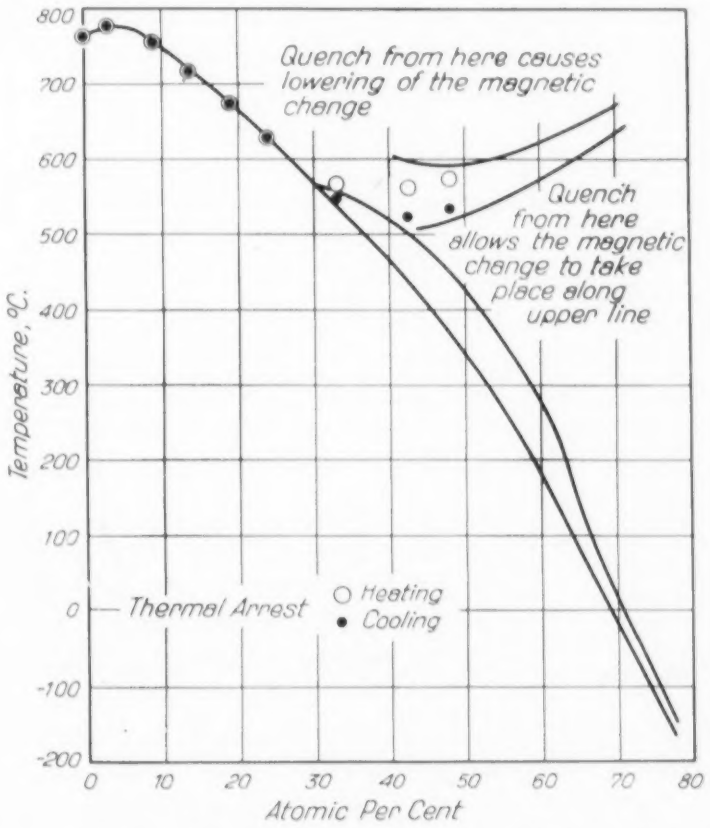

Fig. 7A—Part of the Phase Diagram for Iron-chromium Alloys. (After Adcock).

form, at room temperature, an *uninterrupted* series of solid solutions from iron end to the chromium end. Adcock's interpretation of the diagram is shown in Fig. 7A. The results of dilatometric work by Chevenard (10), the discovery of a "brittle" constituent by Bain and Griffiths (11), and the latest work of Wever and Jellinghaus (12) indicate the formation of an iron-chromium compound, the range of stability for which lies, at room temperature, between chromium concentrations of about thirty-eight and sixty weight per cent.[11] Let us not be distracted, however, by the consideration of a compound: It

[11]Adcock supplementing his own paper (19) questions, with considerable justification, the results of Wever and Jellinghaus.

will be brought into discussion later. With regard to the rest of the system (i.e., from 0 to 38 per cent and beyond 60 per cent chromium), all of the investigators agree that substitutional type of solid solution is formed. Thus, a number of alloys falling, because of the composition, outside of the gamma loop, solidify as alpha-iron-chromium-solid solution (the assertion of Janecke (13), concerning the formation of iron-chromium eutectic, now being discarded) and remain

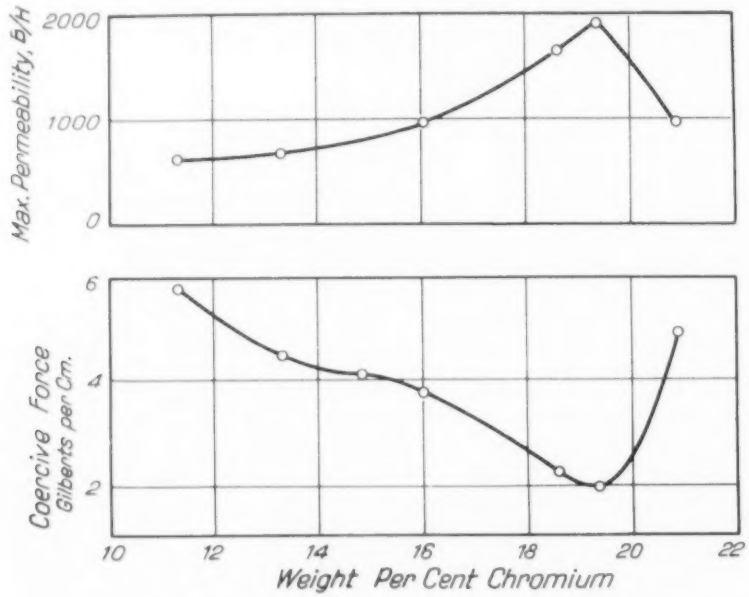

Fig. 8—Magnetic Properties of Iron-chromium Alloys. (After Fischer).

as such upon cooling to room temperature. It is in these alloys of iron with chromium that the *gradual* variation in properties would be expected. The authors of numerous studies, however, submit experimental results difficult to reconcile with the frequently accepted "nature of the alloys."[12] The curve of lattice parameter (Preston's) already shown, and verified on several alloys in my laboratory, exhibits a marked change of slope at about 7 atomic per cent of chromium. Above twenty per cent the numerical data are less consistent, but the other line could conceivably be drawn tangential to the curve at a point corresponding to about twenty-two per cent chromium.

Among the additional data, the magnetic are of interest. Most

[12]In those alloys which undergo allotropic transformation at elevated temperatures the differences in experimental data may be explained by failure to achieve true equilibrium (in the physico-chemical sense) or to take into consideration the "physical condition",—a term which will be explained later. This possibility, however, could not be entertained in connection with "one-phase" alloys.

of the magnetic experiments were concerned with the determination of A_2 or Curie point, the dependence of which upon chromium concentration was shown in the diagram (Fig. 1). The measurements of magnetic permeability, etc., were conducted by Fischer (14) and Preston (18). The results of Fischer, reproduced in part in Fig. 8, show a pronounced maximum for permeability at about 18.5 weight per cent chromium.

Plotting of Preston's data, secured at low magnetizing forces, shows definite scattering of points. With increased magnetization his curves flatten out. The results of these workers do not justify any definite conclusions.[13]

The investigation of electrical resistivity is summarized by Adcock (19) as follows: "Apart from a rather sudden change of curvature at a composition of about twelve per cent chromium the resistivity curve is of the inverted-U type, indicative of the existence of a continuous series of solid solution.[14] Adcock, unfortunately, did not explore the region of most interest—from 18 to 38 per cent chromium.

Dilatometric observation by Murakami[15] and co-workers (28), Chevenard (10), Wever and Jellinghaus (22), amongst the most recent, were confined primarily to the gamma loop region and to the alloys where the formation of a previously mentioned compound was suspected. No attempt was made to explore the region immediately beyond the alpha and gamma region, and furthermore no precautions were taken to ascertain that sufficient time was allowed for the reaction to proceed.[16] As a consequence no conclusion was drawn concerning the alloys of single-phase type.

A striking proof of either an inadequacy of the diagram or of our incomplete picture of the nature of solid solutions and their inherent characteristics comes from the studies of mechanical properties. While strength and ductility (in tension) vary in a normal gradual manner as we progress from one alloy to the other, higher and higher in chromium, toughness (viz, resistance to impact) disappears, for all practical purposes, around 18 per cent chromium. Lest it should be misunderstood, I wish to explain that, by carefully conducted,—we

[13]Magnetic results are affected by so many factors (a paper by Kussman (20) gives an excellent summary) that, in general, magnetic characteristics should not be accepted as an absolute criterion. This, of course, does not diminish their supplementary value.

[14]This appears to be the only investigation on a complete series of comparatively pure alloys. Earlier work of Portevin conducted on alloys contaminated with carbon shows a maximum at about 15-16 per cent chromium (weight).

[15]Secured incidently from alloys high in impurities.

[16]This is a very important factor as will be shown further down.

may even say, "special" treatments, the toughness even at this concentration can be improved,—in itself a very important observation—but that is *not* the point. The fact remains that neither the loss of toughness under normal or ordinary conditions of treatment nor its return after special treatment is explained by the usual concepts of the nature of the alloys.

Experimental Work:

(a) *Preparation of Alloys*

A searching investigation into the innermost essence of metallic bodies is a most formidable task, immeasurably lightened by progressive elimination of possible variables. The influence of even minute amounts of impurities, so well recognized, is one of such variables. It must, regretfully, be admitted that in some of the cases cited the investigated alloys were lacking in purity.[17] Obviously, if additional experimental data were to be sought, they should be secured from a series of alloys in which the impurities were reduced to a minimum. With this purpose in view, extra precautions were taken: The alloys were melted in vacuo, using as ingredients hydrogen-purified iron and the best available electrolytic chromium or ferrochromium, both practically carbon free. The ingots were forged and subsequently homogenized at 1250-1300 degrees Cent. (2280-2370 degrees Fahr.) in argon (from 10 to 20 hours). The final chemical analyses were as follows (Table I):

Table I
Analysis, Weight Per Cent.

Alloy Designation	Chromium	Carbon	Nitrogen	Hydrogen	Oxygen	Other Impurities
F 12	11.82	0.01 0.006	0.004 0.005	Less than 0.0005	0.020	nil
W 14	12.93 12.99	0.01 0.008	0.004 0.005	0.0002	0.046	nil
W 16	14.94 15.04	0.008 0.009	0.003 0.007	0.0006	0.03	nil
F 18	17.50 17.39	0.010 0.010	0.016 0.015	Less than 0.0005	0.031 0.032	nil
F 20	18.13 18.26	0.012 0.009	0.009			nil

Two values in any column for one alloy represent the widest variation in the results of chemical analysis at different parts of the

[17]Fischer and Adcock do not give the detailed analysis for impurities in their alloys, but the materials used in preparation of alloys certainly could not be considered of the highest purity.

forged bars. Such impurities as silicon, manganese, nickel, sulphur, and phosphorus were present merely as "traces," and therefore are not included.

Some concern was caused by unexpectedly high oxygen in several of the alloys. It was ascertained, however, that most of the determined oxygen came from small particles of alumina which became detached from the walls and bottom of the crucibles and were mechanically held within the ingots. When these inclusions were extracted and analyzed, the total oxygen was found to be virtually the same as in corresponding ingots. The metal proper therefore is assumed to be practically oxygen-free. Carbon was as low as was possible to obtain. These alloys will be referred to in future discussion as *carbonless*.

In addition, a series of alloys was made in an Ajax experimental furnace, using the usual procedure for deoxidation, etc. These alloys analyzed as shown in Table II. The available material, is was hoped, would afford an opportunity for the following:

(a) To ascertain the characteristics of fairly pure[18] carbonless alloys, and, thus to judge the adequacy of the diagram.

(b) To establish the parallel, if any, between carbonless and commercial alloys, noting, thereby, the influence of impurities, including carbon.

The ultimate in research work should not only be the answer to the question *what,* but also to the question *how.* The experimental procedure was decided upon with this idea in mind. Impact resistance and hardness (from among mechanical properties),[19] dilatometric observations, microscopic examination and X-rays were selected to ascertain characteristics; age-hardening, followed by microscopic and X-ray study, mechanical characteristics at subnormal and slightly elevated temperatures—to attempt an answer to the question *how.*

(b) *Impact Resistance, Hardness, "Physical Condition"*

Alloys on which impact values were obtained were heat treated in several ways thought to be the best for the purposes of investigation. In each case the relative *trend* was quite the same.

The results are summarized in Fig. 9, in which the alloys are

[18]The remarkable purity attained in iron by Yensen and Ziegler for their studies of magnetic properties, also Ciaffi, justifies this expression.

[19]Complete study of mechanical properties was impossible because of the relatively small amount of available carbonless material.

grouped in accordance with their carbon content, ranging from less than 0.01 to 0.20 of one per cent.

The abrupt disappearance of toughness is just as evident in "carbonless" as in alloys fairly high in carbon. Furthermore, the loss of toughness is not, so far as could be ascertained, gradual, but

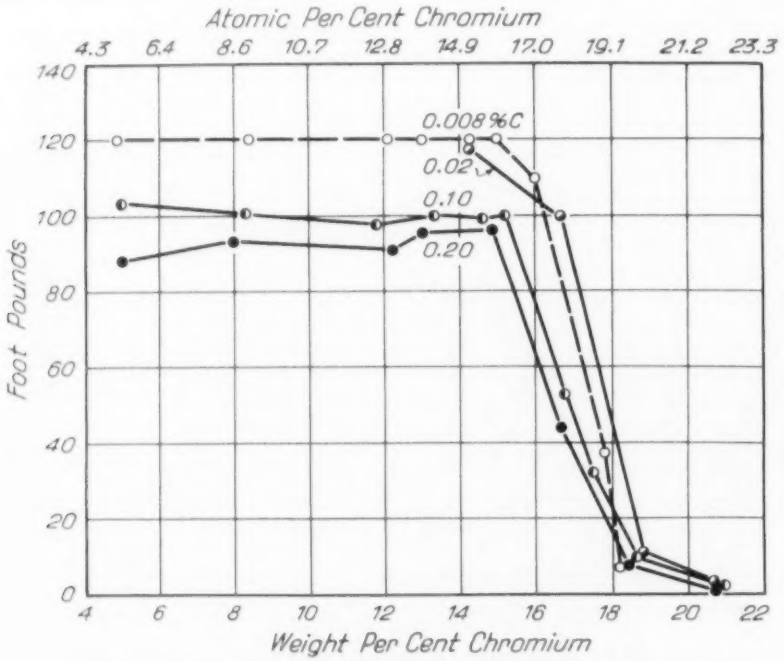

Fig. 9—Impact Properties of Iron-chromium Alloys with Various Carbon Contents. V-notched Standard Charpy Samples.

asserts itself within a very narrow range of chromium concentration, which is substantially the same for all alloys, irrespective of their carbon content.

From these observations it was concluded that purity and, specifically, carbon, play no part in the sudden change of toughness.[20] The explanation should be sought either in some radical change in the constitution of the alloys or in some other factor as yet undiscovered.

Ordinarily, an abrupt change in one mechanical property indicates similar—but not necessarily of the same sign—changes in others: Concurrent loss of ductility and gain of hardness in most of the steels is a well-known illustration. It does not apply, however, to alloys of chromium. In both the very low and the (fairly) high carbon series the change in hardness (with increasing chromium) is

[20]It is not to be inferred from this statement that carbon has no influence at all: It has definite influence in those alloys which lie to the left of that "critical" concentration of chromium where toughness vanishes.

Fig. 10—Unetched Ingot of Vacuum-Melted Carbonless Alloy of Chromium Showing Remarkably Large Beautiful Grains. Natural Size.

gradual and relatively small. Other mechanical properties will be found to vary much in the same manner as hardness (if care is taken to give the alloys proper heat treatment),—Table V.

Technical literature at times makes use of the term "physical condition" by which it is sought to denote certain variations in the "make-up" of the metals and alloys, such as presence or absence of internal stresses, chemical homogeneity, grain-size, distribution of structural constituents, etc.

The effect of varying physical condition on the properties is so well recognized, that every effort was made either to minimize it or to take it into consideration.

Chemical homogeneity and uniform distribution of structural constituents (in alloys consisting of more than one phase) was taken

care of by high temperature homogenizing and repeated mechanical and heat treatments.

An attempt was made, through controlled experimental conditions,—to bring to a minimum internal stresses which may originate either during or at the conclusion of heat treatment.

Internal stresses as a result of atomic distribution and bonding

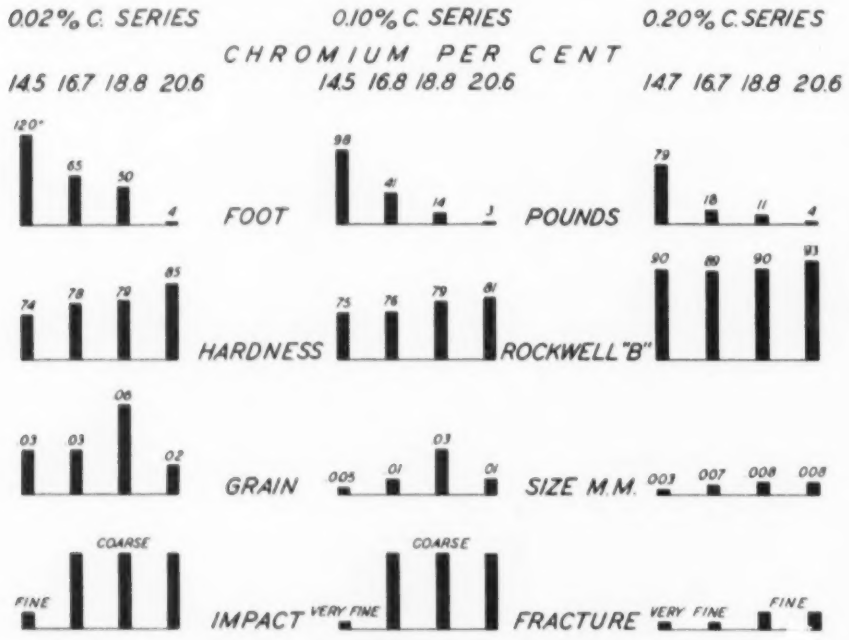

Fig. 11—Diagram Showing the Lack of Relationship between Toughness (Ductility) and Hardness. Also, the Independence of Toughness from Grain-size.

in alloys of variable chromium concentration should not be brought into discussion, considering the inadequate experimental data.

Grain-size is controllable, of definite importance, and, furthermore, measurable. Vacuum-melted carbonless alloys of chromium were made up of remarkable large, beautiful grains, reproduced in Fig. 10.

To break up these grains is no easy matter, but can be accomplished by repeated mechanical working. The fact that sudden drop in toughness is independent of grain-size was clearly demonstrated by testing two alloys with grains averaging respectively 0.2 and 4.0 square millimeters: The results of the tests were, for all practical purposes, identical. That it is true, with certain limitations to be discussed presently, is illustrated in Fig. 11, in which impact values, hardness, and grain-size are reproduced for a series of alloys.

There is no relation, for the same carbon content groups, between impact strength and grain-size. These results must not be, however, misunderstood: We are discussing the abrupt appearance of impact brittleness, and its independence of the grain-size. In a given alloy, if it contains less than a certain critical amount of chromium, the resistance to impact (and, of course, other properties) may be considerably improved by grain refinement, as should be expected. But in alloys, in which the impact brittleness appears to be an inherent characteristic, the grain-size alone is of no consequence.

(c) *X-ray, Microscopic, Dilatometric Studies*

In view of the careful X-ray work, reported in previous investigations, the efforts of our laboratory were confined to checking lattice parameters of one or two alloys. When it was found that our measurements checked those of Preston (see Table IV) further work was discontinued.

Microscopic examination revealed the typical structure of solid solutions, with, apparently, no visible change whatsoever, as we pass from tough to brittle alloys. One observation is worthy of note: Distortion, such as that resulting from cold work, of ferrite and ferrite-bearing steels, is revealed on a polished section by the presence of characteristic wavy strain lines. In the alloys under investigation, strain lines are altogether different,—straight, comparatively few, oftentimes intersecting each other at different angles[21]. Fig. 12. The pertinence of this observation will be discussed later in connection with properties at subnormal temperatures.

Turning our attention now to dilatometric studies, the only justification for reproducing the results of investigation conducted in the usual manner, that is, at a fairly low rate of heating and cooling (6 degrees per minute) lies in the relative purity of the alloys and the desirability of having a basis for comparison with subsequent experiments. Figs. 13 and 14 show the curves for two typical alloys: one in which the phase change is evident and the other held to be lying outside of the gamma loop.

The proof of the phase change occurring in the alloys with 12.99 per cent chromium (Fig. 13) is given by the noted failure of heating and cooling curves to follow the same course, although at the end of the experiment the sample comes to its original dimensions. In

[21]Very similar to the ones observed in iron-silicon alloys.

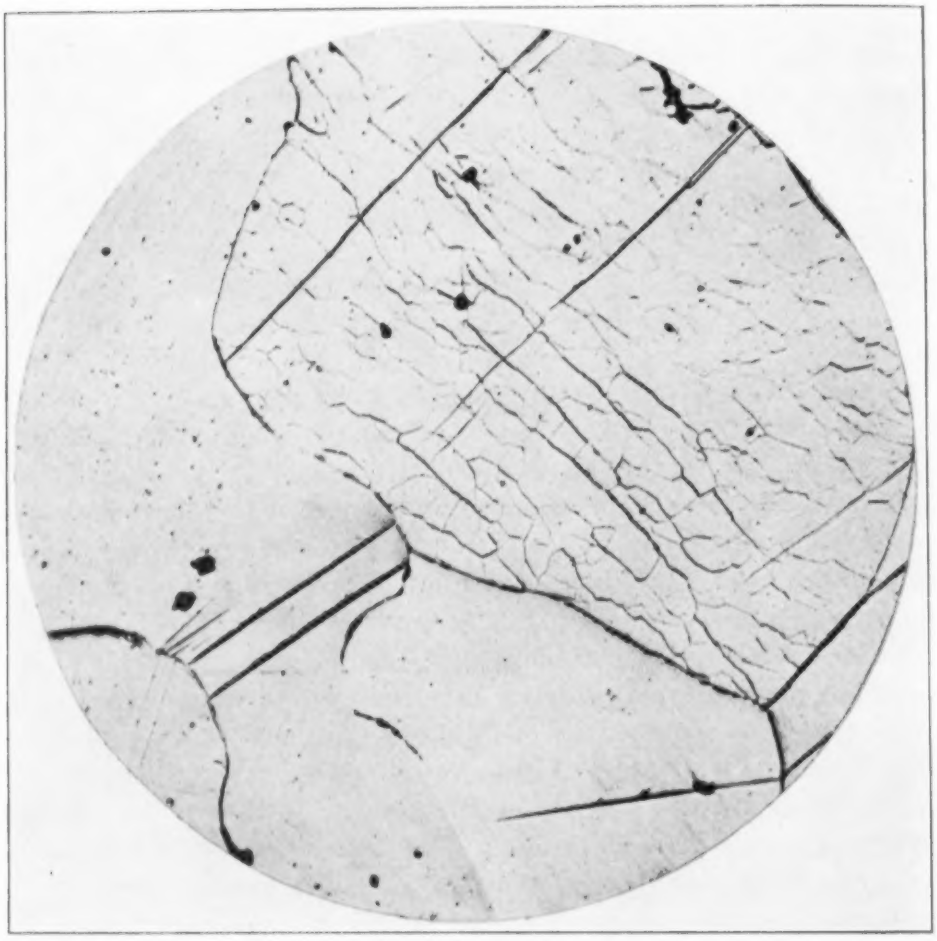

Fig. 12—Photomicrograph Showing the Typical Structure of a Solid Solution. Distortion Due to Cold Work is Revealed by the Presence of Wavy Strain Lines. Ferric Chloride Etch. × 440.

alloys of 15, 17.5, and 18.2 per cent chromium (Fig. 14), however, the path and the slope of the cooling and heating curves are identical. Thus, we may conclude that the end of the gamma loop lies somewhere between 13 and 15 per cent chromium, as generally accepted.

Recent investigations of chromium steels[22] revealed that the rates of transformation in these steels are very low, especially if the transformation does not involve the formation of eutectoid (low carbon steels). Consequently, the conclusion with regard to gamma loop limits, or whatever other information the dilatometric curve may present, will not be justifiable unless the experimental procedure was such as to insure, at any given instant, approach to equilibrium.

In performing dilatometric studies upon alloys in which the re-

[22]Mr. Rush Lincoln in the author's laboratories. As yet unpublished.

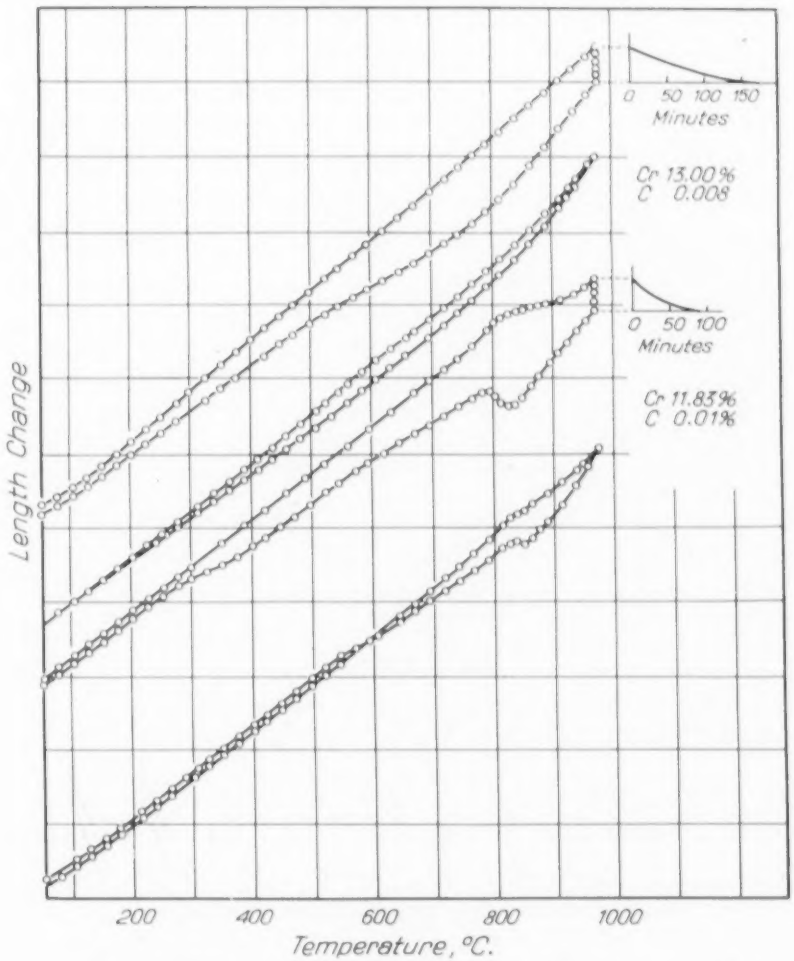

Fig. 13—Dilatometric Curves for Low Carbon Chromium Alloys, Run at 6 Degrees Cent. Per Minute. Also Dilatometric Curve for the Same Alloys After Holding.

action velocity is low, or in which the amount of the transformed phase is small, it is obligatory to use very low rates of heating and cooling. An alternative may be found in subjecting the alloys to "holding" at any selected temperature at which the phase change may be expected. If the expectation is fulfilled and the reaction does proceed at this particular temperature, plotting the change of length against time will give an *approximate* idea of the rate of reaction.

This method was followed with the alloys for which the dilatometric curves were just shown. The alloy of 12.99 per cent chromium, upon holding at 1000 degrees Cent. (1830 degrees Fahr.) for three hours, has undergone definite contraction (Fig. 13)—formation of gamma phase. Subsequent cooling produced a definite

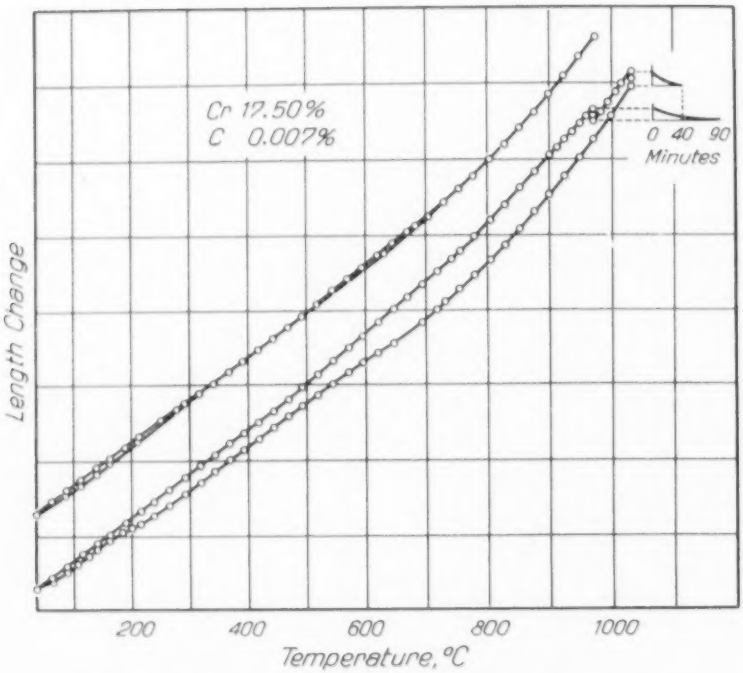

Fig. 14—Dilatometric Curve for Iron-chromium Alloys Run at 6 Degrees Cent. Per Minute and also Holding at High Temperature.

break in the opposite direction,—indicating *slow* transformation of the formed gamma back to alpha. By holding the sample at the temperature corresponding to the beginning of the break as much of the transformation will occur in attaining equilibrium as is allowed by the phase rule. Upon further lowering of the temperature and holding, the transformation will proceed again,—because an alloy of this composition falls within the field of two phases, the relative amounts of which are governed by the temperature.[23]

The fact that this alloy did not come back to its original length can be explained in part by the previous history of the sample: It was not in true equilibrium when the original heating was begun. Similarly performed experiments on alloys with 15.0 and 17.50 per cent chromium yielded, except for magnitude, identical results. Definite contraction of the alloy with 17.50 per cent chromium (Fig. 14) occurring on holding either at 1000 or 1070 degrees Cent. (1830-1960 degrees Fahr.), also the different path (with a pronounced break) of the cooling curve and subsequent return of the sample,

[23]Alloys used for this experiment were thoroughly homogenized. This precaution should dispose of the argument that the observed contraction may be caused by the improved chemical uniformity in process of time.

upon slow cooling, to its original dimensions[24] should be accepted as a well-founded indication of phase change, affecting, in all probability, but a very small portion of the sample.

In the alloy with 18.20 per cent chromium, the magnitude of the transformation at high temperatures was found so small, even after prolonged holding, as to be hardly perceptible.

Without any attempt, at the moment, to explain these experimental results, the conclusions as to laboratory facts are as follows:

(d) *Conclusions Based on Experimental Evidence*

(a) At a certain chromium concentration, alloys of fair purity are characterized by rapid modifications in some of their properties. This change is not governed either by carbon percentage or by impurities in the ordinary sense of the word.

(b) Further, these alloys, contrary to orthodox understanding (the Curie or magnetic point is not considered), undergo some transformation which may or may not be a simple phase change (alpha to gamma and reverse).

Disregarding the philosophic difficulties of causes and effects, it is much easier in the course of an investigation to observe certain effects than to uncover underlying causes. However true that may be, it must also be remembered that without causes there would not be any effects.

(e) *Further Experimental Work: Age Hardening*

"Causes," as we understand them at present, imply:

(1) The appearance of a new phase.

(2) Possible polymorphic transformations.

(3) The separation of even minute amounts of impurities, and, finally,

(4) A somewhat broadly used expression "a change in the *nature* of either solvent or solute."

So very little work has been done on the last mentioned possibility that the understanding of it largely borders on speculation. For this reason alone its discussion will be avoided as much as possible.

"There appears to be no question," states Merica in his admirable treatise on age hardening,[25] "that the atomic changes which occur

[24] If the rate of cooling is high the cooling curve will cross the heating and the sample would finish with smaller length. This should not be taken, however, as a proof for retention of gamma: We are dealing with volume and not with length change.

[25] Paul D. Merica, *"The Age Hardening of Metals"* (21).

Table II
Analysis, Weight Per Cent

Heat No.	Carbon	Manganese	Silicon	Phosphorus	Sulphur	Chromium	Nickel
L-1168	0.030/.030	0.39	0.20	0.011	0.013	14.28	0.10
L-1169	0.098/.104	0.28	0.31	0.013	0.010	14.63	0.10
L-1170	0.194/.196	0.35	0.30	0.010	0.013	14.74	0.11
L-1171	0.023/.025	0.35	0.27	0.010	0.014	16.66	1.10
L-1172	0.103/.104	0.35	0.29	0.011	0.011	16.84	0.12
L-1173	0.147/.148	0.31	0.26	0.012	0.015	16.56	0.14
L-1174	0.191/.191	0.35	0.29	0.006	0.013	16.74	0.14
L-1175	0.021/.023	0.37	0.32	0.008	0.013	18.84	0.13
L-1176	0.102/.103	0.36	0.27	0.010	0.008	18.84	0.17
L-1177	0.155/.158	0.34	0.32	0.011	0.010	18.55	0.14
L-1178	0.202/.207	0.36	0.30	0.010	0.014	18.77	0.16
L-1179	0.028/.032	0.35	0.25	0.010	0.012	20.61	0.15
L-1180	0.078/.082	0.35	0.34	0.011	0.009	20.68	0.18

during (age) hardening, and which, therefore, may be said to cause it, are the direct result of the instability of a supersaturated solid solution and of its gradual decomposition in some manner during aging."

This assertion is based on extensive studies of many different metallic systems. It is quite reasonable, therefore, to assert that experiments which might ascertain the susceptibility of chromium alloys to age hardening should yield those essential data needed to arrive at a conclusion regarding the equilibria of the system.

In accordance with this belief, the whole series of alloys, of the compositions listed in Tables I and II, were investigated for age hardening. First the alloys were thoroughly homogenized, subsequently reheated to either 1450 or 1950 degrees Fahr. (790-1065 degrees Cent.) cooled in still air and finally aged at 840 degrees Fahr. (450 degrees Cent.) and 915 degrees Fahr (490 degrees Cent.) for periods up to 425 hours.[26]

The results, divided into groups according to carbon content, are graphically reproduced in Figs. 15 through 19.

Of utmost interest are the results on alloys with less than 0.01 per cent (small amounts of carbon present, are, undoubtedly, less than the limit of solid solubility at the temperature of aging) and with 0.02 per cent carbon. And while "0.02 alloys" not having been prepared for this particular part of the investigation, contain sufficient impurities to cause some concern, the "less than 0.01 per cent carbon" alloys are sufficiently pure to be free from this objection.

Carbonless alloys show a most pronounced and definite tendency to age harden: (Fig. 15). Since the details can be learned from the

[26]To provide additional data holding time at 1450 or 1950 degrees Fahr. was varied from 1 to 3 hours: this variation did not seem to have much influence on the final results.

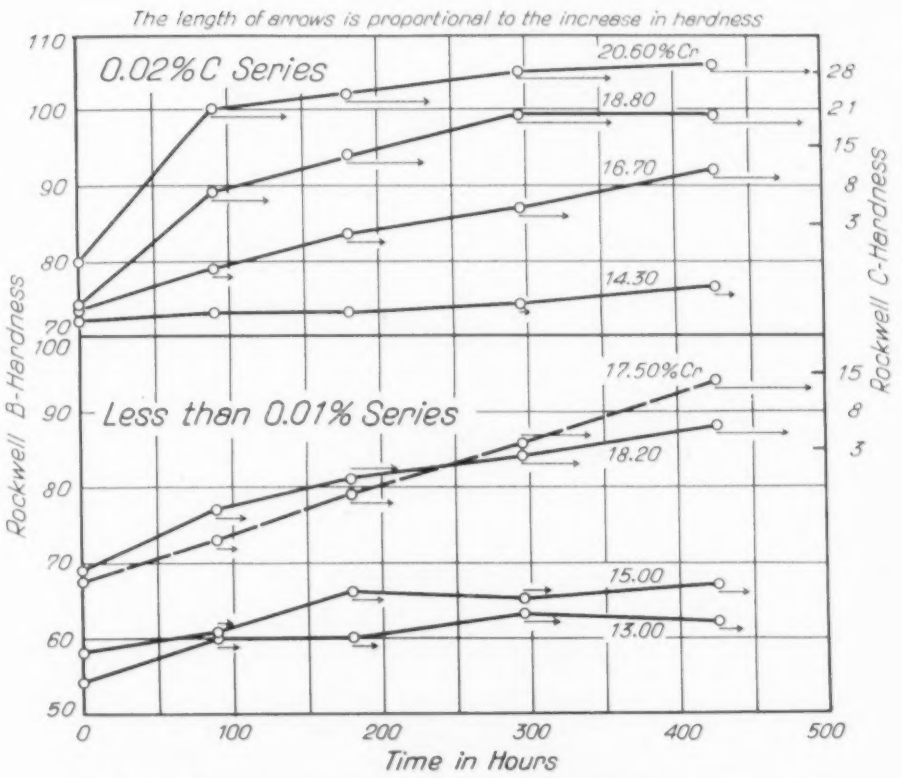

Fig. 15—Diagram Showing the Age-hardening Phenomenon in Iron-chromium Alloys.

numerous curves, it will suffice to state that the total increase in hardness for an alloy with 18.20 per cent chromium was, at the end of 425 hours, 26 points on Rockwell "B" scale and the same carbonless alloy with 17.50 per cent chromium showed an increase of 19 points. At the same time, alloys with about 13 and 15 per cent chromium showed much less, in fact, very little tendency to harden.

Similar, almost quantitatively identical, results were obtained on other series of the same alloys, aged under varied conditions. It appears to be quite definitely established that the age hardening property is *directly proportional to chromium concentration,*[27] within the limits studied.

The same is true of the alloys with 0.02 per cent carbon: (Fig. 15). The comparison of both series will convince you that for all

[27]This *definite* proportionality between the degree of age hardening and chromium content disposes, quite decisively, of the remote, but nevertheless realized, possibility that aging might have been caused by the impurities present in the alloys. (See Table I for analysis.)

Unfortunately no data on aging of Cr-Fe alloys, containing variable percentage of oxygen and nitrogen, could be found. The effect of aging, produced in *iron* by amounts of O_2 and N_2 similar to those in Table I, is definitely less.

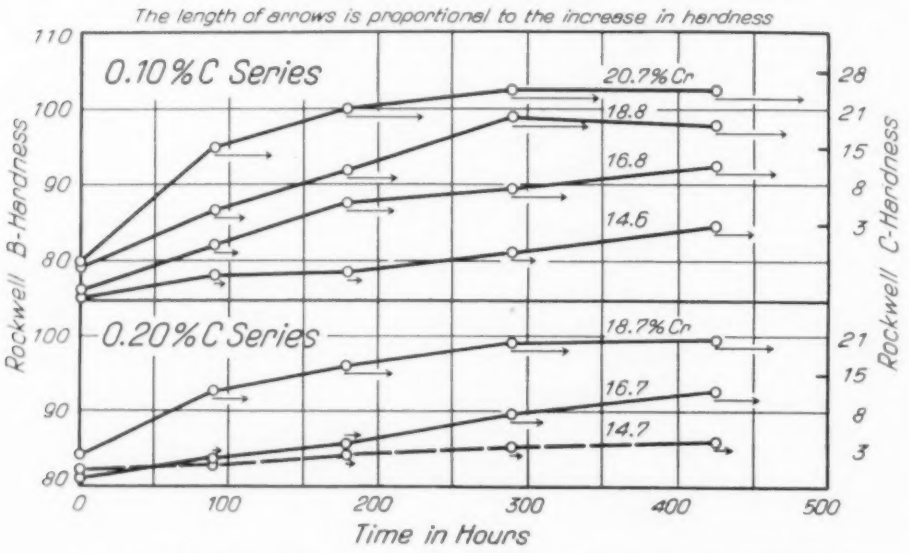

Fig. 16—Diagram Showing the Age-hardening Phenomenon in Iron-chromium-carbon Alloys.

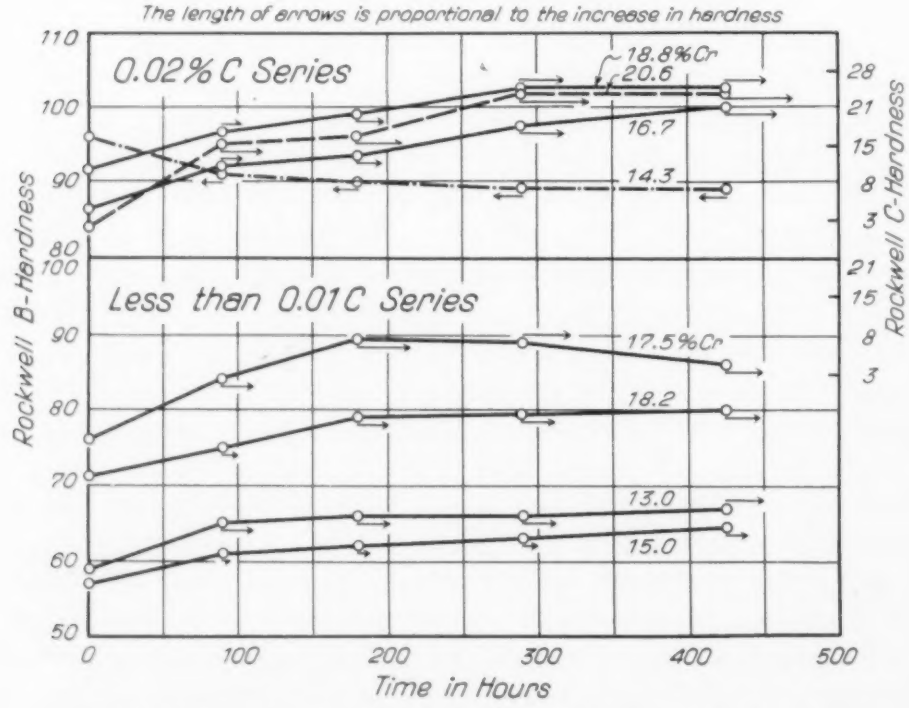

Fig. 17—Diagram Showing the Age-hardening Phenomenon in Iron-chromium Alloys.

practical purposes the same "total increase in hardness" (for corresponding chromium contents) has been obtained. Slight differences in the behavior were confined to the observations that "0.02" series

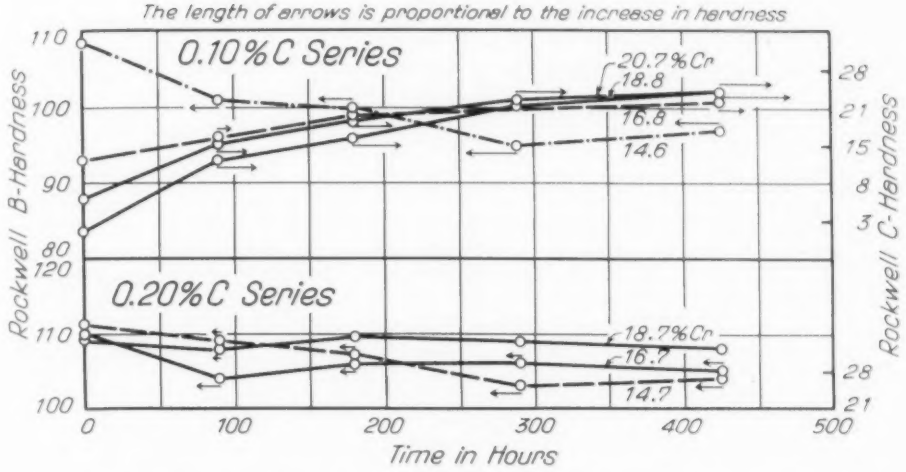

Fig. 18—Diagram Showing the Age-hardening Phenomenon in Iron-chromium-carbon Alloys.

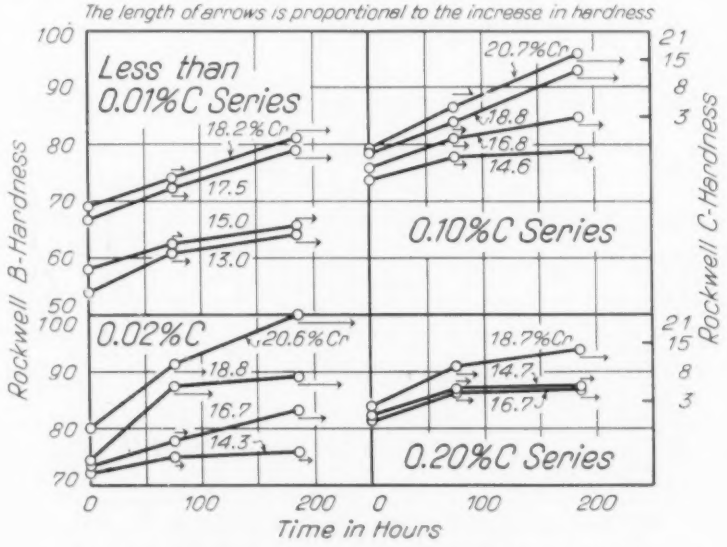

Fig. 19—Diagram Showing the Age-hardening Phenomenon in Iron-chromium and Iron-chromium-carbon Alloys.

were definitely harder at the beginning and seemed to react somewhat faster at the start of the experiment.

The fact that alloys air-quenched, prior to aging, from 1950 degrees Fahr. (1060 degrees Cent.) show much less susceptibility to age hardening (Fig. 17) than if quenched from 1450 degrees Fahr. (787 degrees Cent.) becomes quite significant in the light of already discussed dilatometric work. If, as it was suggested, some gamma iron is formed in alloys with 17.50 and 18.20 per cent chromium, upon heating to high temperature, air cooling of the sample will cause some gamma to forego its complete transformation with consequent

increase in initial hardness. Aging would tend to decrease the hardness of this gamma, thus diminishing the total effect of the age-hardening process.[28]

Additional data on susceptibility to age-hardening with accompanying change in resistance to impact is contained in Table III. The

Table III

Sample No.	Analysis Per Cent Carbon	Analysis Per Cent Chromium	Impact, foot pounds. Heated to 1450°F. for 3 hours, air cooled	Impact, foot pounds. Heated to 1450°F. for 3 hours, aged at 914°F. for 200 hours
68	0.03	14.28	175	129
70	0.19	14.74	34	62
71	0.02	16.66	132	4
74	0.19	16.74	44	25
75	0.02	18.84	85	2
76	0.10	18.84	73	3
78	0.20	18.77	12	3
79	0.03	20.61	11	2
80	0.08	20.68	7	2

experiment was deliberately confined to the alloys made in the orthodox way. The loss of resistance to impact in the alloys between 16 and 19 per cent chromium with 0.02 per cent carbon is quite astounding.

(g) *Discussion*

I admit that it was with deliberation when I spoke just a few minutes ago, of observed effects and the difficulties in uncovering underlying causes. The aging of chromium alloys is an effect. You will probably agree with me that the explanation is neither simple nor obvious. The questions to which I should like to have a definite answer would be: (a) What is the actual process of age hardening in iron-chromium alloys? (b) Is it a true case of precipitation hardening and if so what is the precipitated constituent?

In one of the preceding slides (Fig. 1) was presented an iron chromium diagram in which a compound, capable of dissolving either chromium or iron, was shown. The field occupied by this compound at room temperature is restricted to concentrations, approximately, from 38 per cent to 58 per cent chromium; the field becomes nar-

[28]With the increasing carbon content the hardenability of alloys upon aging is definitely decreased (Fig. 18), although in 18 and 20 per cent chromium with 0.10 per cent carbon it is still quite evident. These alloys, however, are supersaturated with carbon at aging temperature, and it is natural to expect certain deviations in the behavior of these alloys. With still higher carbon or with raised initial hardening temperature the allotropic changes enter into the picture and affect the results in the manner which could have been predicted.

rower with rising temperature and the compound is shown to disappear above approximately 930 degrees Cent. (1705 degrees Fahr.) Wever and Jellinghaus (17), who claim to have established the formation of this compound by means of microscopic, X-ray, and dilatometric analysis, assign to it the formula FeCr, basing their conclusion on the identity of the obtained X-ray pattern with that for FeV,—a compound, by the way, which needs more confirmation than is available. Earlier, the probability of a compound was indicated by Chevenard (10), Kreutzer (16), Bain and Griffiths (11), also, in another publication, by Wever and Jellinghaus (22).

Speaking of this compound Wever and Jellinghaus say: " . . . compound FeCr forms from solid solution with very low velocity."[29] Four days of heating at 600 degrees Cent. were required in order to obtain an appreciable amount of the compound in the alloys of 40 and 50 per cent chromium. It is thus explained why earlier investigators failed to discover it.

Assumption of the existence of the compound within certain limits of concentration suggests an explanation, admittedly speculative, of age hardening: Is it not possible that with much prolonged time of heating (approach to equilibrium) the limits of compound formation may be found to extend far beyond those sketched at present?

The indisputable proof would have been forthcoming if it could be shown that the samples of 16 to 20 per cent chromium aged for 425 hours (or approximately 18 days) contained the compound FeCr in equilibrium with iron-chromium solid solution.

By means of X-rays, using a back-reflection (Sachs) camera and $K\alpha$ chromium radiation, several alloys were investigated. No new lines appeared in the aged samples and their photograms were identical with those for unaged samples. The lines in the aged samples were found to be somewhat more diffuse, but the difference was not sufficient to be considered as significant. The measurements of the lattice parameter before and after aging are recorded in Table IV and will be found unchanged, making allowances for experimental error.

The results of microscopic examination were equally negative. Although the aged samples appeared to be reacting toward etching reagents somewhat differently and, at times an anxious eye believed

[29] "Im Zweistoffsystem Eisen Chrom wird eine Verbindung FeCr nachgewiesen die sich mit sehr *geringer Geschwindigheit* aus dem Mischkristall bildet." Reference 17, page 147.

Table IV

Alloy No.	Chromium	Treatment	Hardness Rockwell "B"	Lattice Parameter A°	Lattice Parameter according to Preston[18] A°
F18-I	17.50	One hour at 1950°F. air cooled.	70.0	2.8683	2.867
F18-H	17.50	One hour at 1950°F. air cooled, aged at 914°F. for 425 hours.	80.0	2.8681	
F18-C	17.50	One hour at 1450°F. air cooled.	67.5	2.8683	
F18-B	17.50	One hour at 1450°F. air cooled, aged at 914°F. for 425 hours.	94.0	2.8689	
W14-C	12.93	One hour at 1450°F. air cooled.	55.0	2.8675 2.8676	
W14-B	12.93	One hour at 1450°F. air cooled, aged at 914°F. for 425 hours.	61.0	2.8680 2.8680	

that it was seeing small agglomerations of precipitate, especially at grain boundaries or slip planes, the hoped for and conclusive evidence was not found. Of course, it is not altogether surprising. In the first place, the aging phenomenon is not necessarily caused or accompanied by precipitation in the ordinary sense—a well known example being duralumin. These observations made Dr. Merica caution, quoting him again, that "age hardening may also occur in consequence of some structural alteration other than that of the precipitation of excess solute." But even if we *assume,*—at present we would not be justified to use any other word,—that age hardening of chromium-iron alloys is caused by *actual precipitation* of a constituent—the amount and the degrees of agglomeration must be considerable before it would be detected either by microscope or by X-rays.

It is again timely to summarize more specifically the described observations. (a) In the particular case of iron-chromium alloys, experimental observations favor the assumption that the observed volume change is caused by a polymorphic transformation. In other words, that the "gamma-plus-alpha" region (the end of the gamma loop) extends to higher concentrations of chromium than is generally mentioned. (b) The allotropic transformation (alpha to gamma and reverse) proceeds very slowly and the phase equilibrium is attained with difficulty. Whether, upon rapid cooling, any gamma iron as such is, or may be, retained at room temperature, is not possible to state. (c) Aging experiments provide further illustration of

the changes that take place in the supposedly one-phase (solid solution) region.

These experimental results belong to the first two of the four possible reasons mentioned a while ago, namely (a) phase change, (b) formation of a new phase,[30] (c) change in nature of solution and (d) impurities, which would account for the experimentally determined irregularities in properties of one-phase alloys. And since the first two[31] ordinarily mean approach to equilibrium,—a condition from which there is no tendency to depart even though atomic mobility is high, no caution is required in stating this general conclusion: Iron-chromium alloys accepted to be one-phase alloys do not meet the definition of equilibrium. In other words, under normally practiced conditions of treatment, they should be described as "unstable." Illuminating and indeed important as it is to have this conclusion it should not be taken as meaning that the problem is solved. Indeed not. Many pertinent questions and observations, too numerous to be stated here, cannot be satisfactorily answered by the above conclusion. For example, neither the retention of small amounts of gamma iron nor the possibility of precipitation would satisfactorily explain the observed sharp break in impact toughness.[32] Furthermore, it is fully realized that the discontinuities in properties, as shown by this particular method of testing, do not necessarily have to be accounted for on the basis of physico-chemical changes. The impact brittleness of some metals at sub-zero temperatures, definitely known to be independent of any phase change, is well known. The analogy between this phenomenon and the behavior of iron-chromium alloys appeared to be rather striking. Additional experimental work was thought to be justifiable and to it we will now turn our attention.

As an example of the problem before us should be cited the case of iron. Hadfield (31) observed that iron lost its ductility in *tension* at —183 degrees Cent. Sauerwaldt, Schmidt, and Krämer (32) report that low carbon steel becomes brittle, again in tension, at about —155 degrees Cent. A similar statement is made by Russell (33) and concerns medium carbon steel.

Goerens and Mailänder's results, confirmed in general by those of the writer,[33] show the loss of *impact ductility* of iron between

[30]Thermodynamically (a) and (b) are identical.

[31]Whether the third should be also included is a matter of conjecture.

[32]I feel it would be out of place to discuss reasons for this assertion.

[33]A paper by Guillet and Cournot (36) gives lower temperature values (for electrolytic iron) than just cited.

—5 and —30 degrees Cent., depending upon the quality of iron and its previous history.

Thus, iron (and steel) will show, at —5 degrees Cent. or thereabouts, ductility in tension and brittleness in impact.

The important fact already stressed that this phenomenon cannot be caused by any permanent phase change is proved by the return of impact ductility when iron (or steel) is tested, subsequent to refrigeration, at room temperature.

The explanation of this unique occurrence is by no means simple. And of course it was not expected that the investigation of

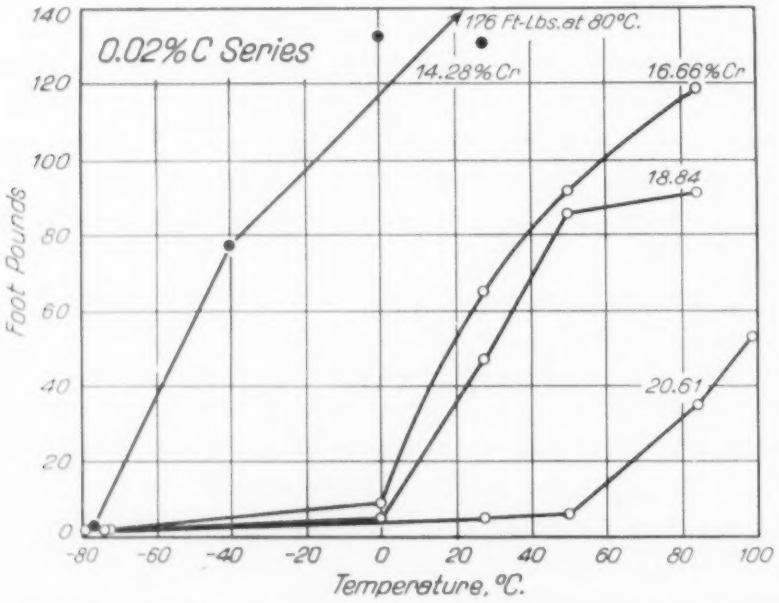

Fig. 20—Diagram Showing the Impact Properties of Low Carbon Iron-chromium Alloys at Sub-zero and Slightly Elevated Temperatures.

mechanical properties of iron-chromium alloys, or rather their variation,—at subzero and slightly elevated temperatures, would disclose the underlying theoretic reasons for this complex question. It was merely hoped to collect further data pertaining to the system under discussion, and, thus, further point out the complexity of the subject and the compelling necessity for additional work in this field.

In executing this part of the investigation, alloys as listed in Tables I and II were tested for impact at *several* temperatures between —76 and +90 degrees Cent., while tensile properties were ascertained only at two temperatures: —76 and +30 degrees Cent. (room). All the tests were made *at temperature*. The results are

Table V

Sample	Carbon Per Cent	Chromium Per Cent	Tempt. of Test—°C	Y.P. lbs/in²	U.S. lbs/in²	% Elong. in 2 in.	% Reduc. Area	Impact Modified Charpy ft. lb.
68	0.030	14.28	—70	43,300	78,700	37		2.5
68	0.030	14.28	26	34,500	65,500	35	70	120.0
69	0.01	14.63	—70	96,500?	98,700	34	71	
69	0.01	14.63	26	49,400	82,500	28	73	98.0
70	0.195	14.74	—70	69,000	105,200	33		17.0
70	0.195	14.74	26		88,000	33	70	85.0
71	0.024	16.66	—70	52,700	79,800	36	70	2.0
71	0.024	16.66	26	34,500	64,700	34	74	65.0
72	0.103	16.84	—70	48,000	87,400	38		
72	0.103	16.84	26	39,400	73,000	32	72	42.0
73	0.147	16.56	—70	56,600	93,500	32	66	
73	0.147	16.56	26	47,500	81,500	29	67	37.0
74	0.191	16.74	—70	63,400	95,800	34		3.0
74	0.191	16.74	26	46,200	81,300	27	67	18.0
75	0.022	18.84	—70	48,800	75,400	15*	13	2.0
75	0.022	18.84	26	45,800	64,500	31	69	30.0
76	0.102	18.84	—70	61,600	90,600	33	63	
76	0.102	18.84	26	44,400	78,600	29	66	10.0
77	0.156	18.55	—70	59,000	94,300	15*	13	
77	0.156	18.55	26	45,500	79,700	26	68	6.0
77	0.156	18.55	26	44,800	79,300	29	68	
78	0.205	18.77	—70	85,100	98,800	28		1.5
78	0.205	18.77	—70	68,400	101,000	29	60	1.5
78	0.205	18.77	26	49,700	83,200	28	67	9.0
79	0.030	20.61	—70	67,400	83,800	23		2.0
79	0.030	20.61	26	42,800	67,400	29	68	5.0
80	0.080	20.68	—70	60.100	90,100	33	63	
80	0.080	20.68	28	49,500	74,600	28	70	4.0

*Broke in threads.

summarized in Table V and are graphically shown in Figs. 20 through 24.

The ductility *in tension is not* adversely affected by refrigeration to —76 degrees Cent. In fact, in the majority of cases it is slightly improved, in spite of noticeably increased tensile strength (the latter observation is general for all tested alloys). But the ductility as measured by *impact* varies within unexpectedly wide limits, regardless, it seems, of carbon content and of previous heat treatment.[34]

More specifically, the following observations concerning impact properties are justified by the evidence. At —76 degrees Cent. *all of the alloys* are exceedingly brittle. At room temperature (30 degrees Cent.) sharp demarcation between ductility and brittleness occurs somewhere between 16.75 and 18 per cent chro-

[34]Various heat treatments were given to these alloys prior to testing. In writing a paper of this sort it is most difficult to be exact in expressing oneself. The last statement means that the variation in results with temperature of testing is of the same tendency, but not necessarily of the same order. Furthermore, the heat treatment given the alloys prior to testing was not in some cases the best to develop toughness, but it is the one which accentuates the described phenomenon.

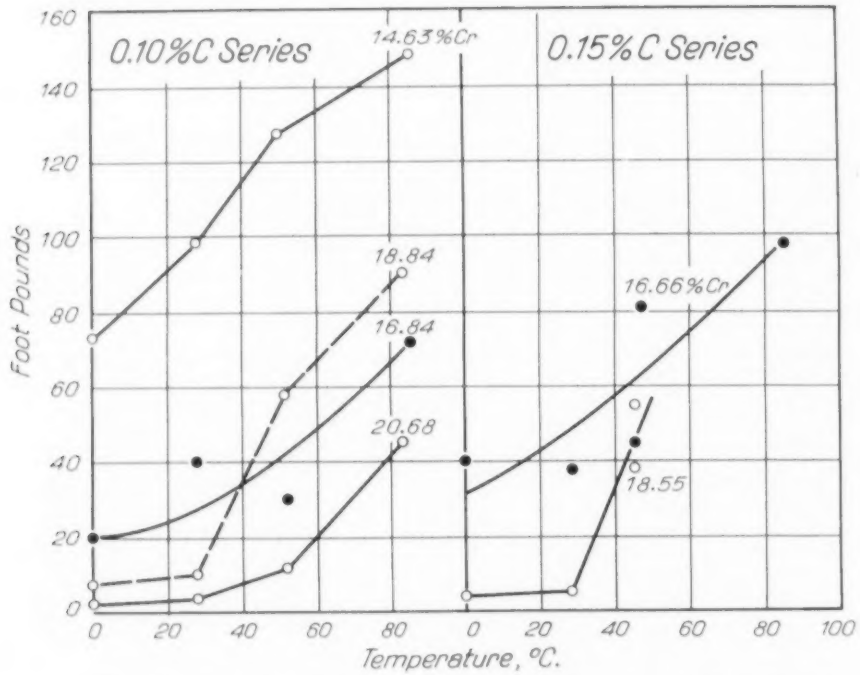

Fig. 21—Diagram Showing the Impact Properties of Iron-chromium-carbon Alloys at Zero Degrees Cent. and Slightly Elevated Temperatures.

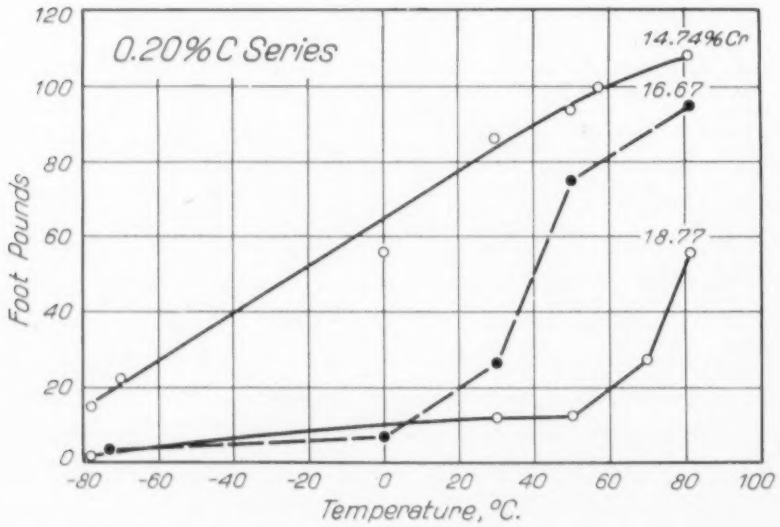

Fig 22—Diagram Showing Impact Properties of Iron-chromium-carbon Alloys at Sub-zero Degrees Cent. and Slightly Elevated Temperatures.

mium.[35] At 50 degrees Cent. carbonless alloys remain practically unchanged, but those containing carbon and with 33 per cent chro-

[35]Note the stipulation on page 15 concerning this statement.

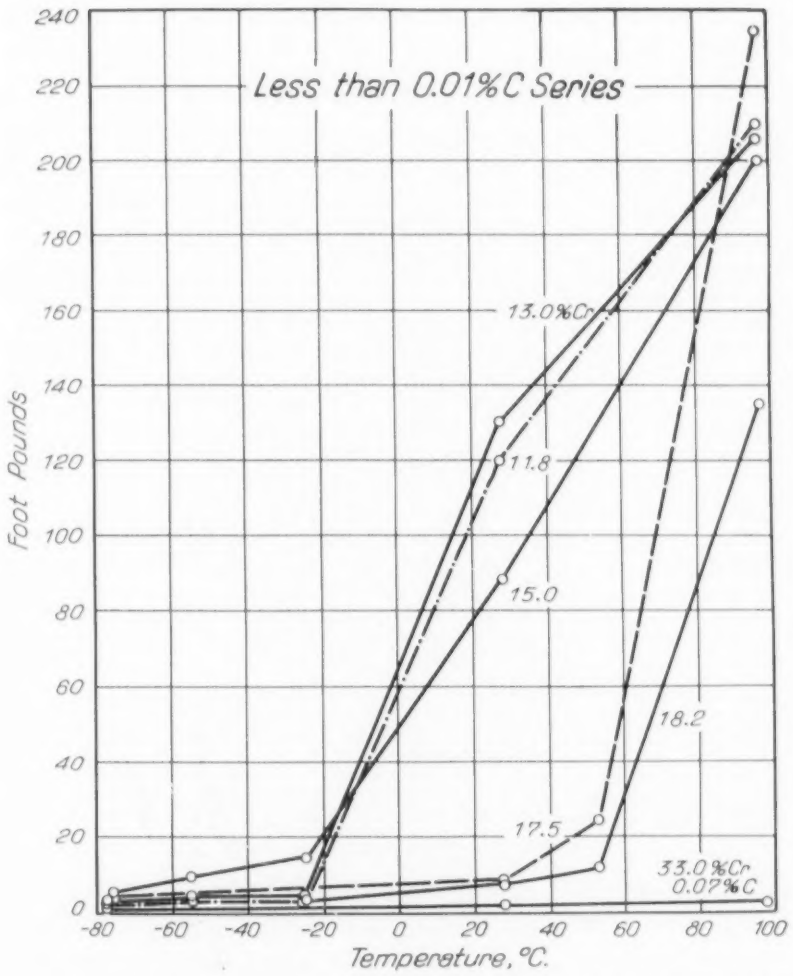

Fig. 23—Diagram Showing Impact Characteristics of Carbonless Iron-chromium Alloys at Sub-zero Degrees Cent. and Slightly Elevated Temperatures.

mium is hopelessly brittle.[36] In other words, the higher is the chromium content the higher is the temperature at which ductility is regained.[37]

These observations, it will be agreed, parallel these of iron, providing that it is ascertained that no change of physico-chemical nature (polymorphic modification, appearance of a new phase) has taken place at low temperatures. Accordingly, alloys were immersed in a liquid at —78 degrees Cent., held for half an hour (time sufficient to produce brittleness if tested at this temperature), removed, and

[36]No alloys with chromium between 21 and 33 per cent were investigated. Hence the "demarcation" composition at 90 degrees Cent. is not known.

[37]The precaution was again taken to determine that such extraneous circumstances as grain-size played no part in this phenomenon.

broken next day at room (30 degrees Cent.) temperature. Results were as follows: (Table VI).

The reversibility of impact "brittleness" and the impact "toughness" (ductility) with the temperature of test obviously excludes the possibility of a permanent change in the alloy at least within the periods used for either refrigeration or treatment in boiling water.

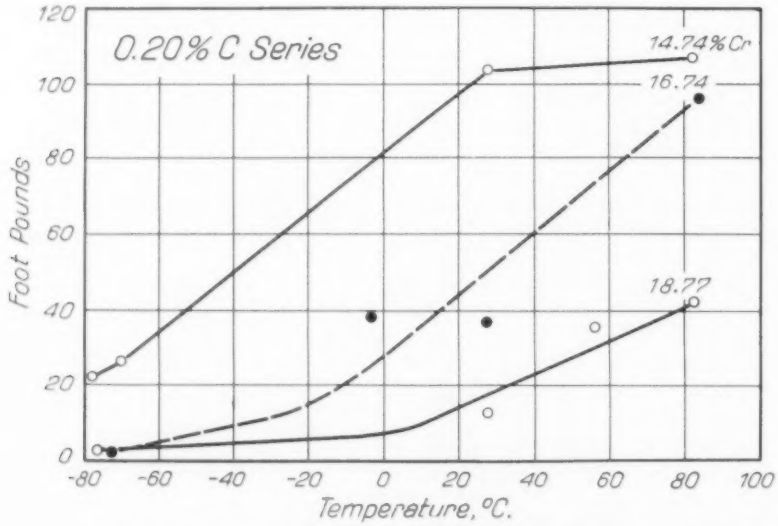

Fig. 24—Diagram Showing Impact Properties of Iron-chromium-carbon Alloys at Sub-zero Degrees Cent. and Slightly Elevated Temperatures.

It would be exceedingly interesting to ascertain the influence of much longer holding at sub-zero or slightly elevated temperatures on the properties of alloys.[38] But this would constitute another problem.

Wherein, then, lies the explanation for the observed intricate behavior of chromium-iron alloys? Any metal or alloy yields to stresses through cleavage, slip, and twinning. It should therefore be

Table VI

			Impact resistance in Foot pounds (modified Charpy)				
	Composition						
Alloy No.	Chromium Per Cent.	Carbon Per Cent.	Broken at 30°C.	Heated to 92°C. broken at 92°C.	Heated to 92°C. held 3 hours, cooled, broken at 30°C.	Refrigerated to —78°C. & broken	Refrigerated to —78°C. broken at 30°C.
F12	11.82	0.010	120.0			2.5	182.0
W14	12.96	0.008	130.0			3.0	132.0
W16	14.95	0.008	88.0			5.0	74.0
F18	17.50	0.010	8.5	234.0	12.0		
F20	18.20	0.012	8.0	135.0	7.0		

[38]Will the temperature of boiling water induce precipitation hardening?

suggested that the resistance of any metal or alloy to rupture is determined by its characteristic cohesive strength (ideal resistance to cleavage) and its resistance to slip (shear).[39] The relative efficiency of these resistances determines the alloy's properties, that is, either toughness or brittleness. With the *changing* temperature of test, the relative values for the two mentioned resistances do not remain the same. This is, of course, an explanation well known to those who have studied this particular subject. Extending this reasoning to the properties of iron-chromium alloys at room temperature it may perhaps be suggested that changing chemical composition in the series of binary alloys produces the same effect as the described influence of the temperature of test. An interesting observation pertinent to the discussion will be found in the two following illustrations: Fig. 25 shows the structure at the break of alloy W-16 (chromium 14.95 per cent, carbon 0.008 per cent), the latter developing 200 foot-pounds impact resistance at 92 degrees Cent. Wavy appearance of the strain lines can be seen. The same alloy broken at —78 degrees Cent. (5 foot-pounds impact resistance) shows no distortion (slip) at all, even at the very edge of the broken part (Fig. 26). Quite similarly, alloys which show either ductility or brittleness at room temperature (depending, as was described, upon their composition) exhibit the same structural characteristics. Would it be far too speculative to suggest —as a possible explanation,—the dependence of cleavage and slip resistance at room temperature upon the distortion of the parent lattice through introduction of foreign atoms? What would be the effect of the manner of distribution of participating atoms within metallic bodies?[40] All these possibilities should affect the manner of "binding" or "bonding" between atoms—the circumstance previously termed as "the change in the nature of solid solution." But all of them constitute at present terra incognita.

The last topic to come under discussion was broadly termed "impurities."

Among the impurities in metals and alloys should be listed such gaseous elements as oxygen, hydrogen, and nitrogen. Alloys of iron and chromium, prepared with such infinite pains on the part of my collaborator in experimental work, Mr. Rush Lincoln, contained very small amounts of the above mentioned elements. That they could have an influence upon the phenomena described should be adjudged

[39]Twinning is accomplished by shearing movement.

[40]For detailed discussion see "Intermetallic Solid Solutions" by E. R. Jette (30).

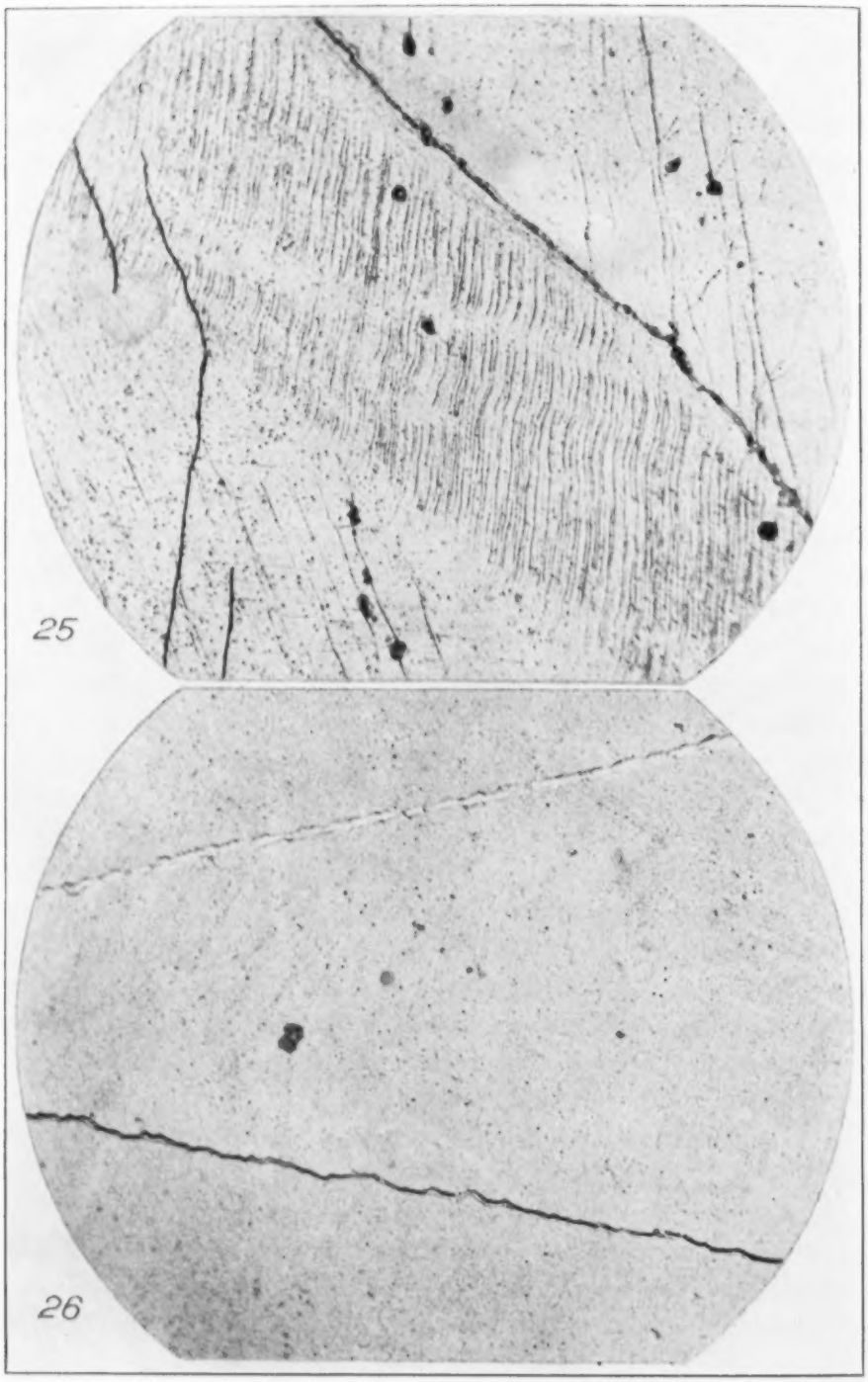

Fig. 25—Photomicrograph of the Structure at the Break of Alloy W-16 Containing 14.95 Per Cent Chromium and 0.008 Per Cent Carbon. × 450.

Fig. 26—Photomicrograph of the Same Alloy as Fig. 25. Broken at —78 Degrees Cent. Shows No Distortion. × 450.

most unlikely. Thus, instead of attempting to reduce further the impurities,—confining this expression to oxygen, hydrogen, and nitrogen, it was decided to study the influence of their increasing amounts. Of these three, nitrogen has recently received some prominence and its study in relation to ferrous alloys was undertaken first. The information revealed by a few preliminary experiments justified continuation of the work. And so, the discussion of impurities is reduced to the discussion of nitrogen in iron-chromium alloys, leaving the question of other gases for some future communication.

While the general subject of gases in iron-carbon steels and non-ferrous metals and alloys has been extensively studied[41]—the interaction between special alloys (including alloy steels) and gases received only scant attention.

It is not unreasonable to anticipate that the tendency of a certain alloy to absorb a gaseous element or to combine with it[42] will be determined to a large extent by the same tendency on the part of the metals making up an alloy. Iron has a notoriously low capacity for absorbing nitrogen. Even at high temperatures and pressures the maximum nitrogen found in iron is from 0.005 to 0.04 per cent (by weight, the latter figure at the melting point).[43] The figures for hydrogen, according to Sieverts (39) and Martin (40) are also very low, even lower than for nitrogen. Among other metallic elements molybdenum will take up very little hydrogen and virtually no nitrogen, which is also true of cobalt and tungsten. Much difference of opinion exists regarding silicon and the influence of increasing amounts of silicon in iron on its absorbing, or as Martin calls it "occluding," capacity for both nitrogen and hydrogen. The behavior of manganese is also debatable, but this much can be said: It was observed in our laboratories that during the attempt to remelt previously distilled manganese under an atmosphere of non-purified argon, the manganese picked up some nitrogen which was present in small amounts in the argon. The element chromium, however, has an astounding affinity for nitrogen, with the strong probability that a nitride is formed. The procedure of introducing nitrogen into chromium is simple and can be varied. Hüttig and Brodkorb (41) have done it by heating metallic chromium in nitrogen to above 550 degrees Cent. (1020 de-

[41]An excellent bibliography will be found in *Metals and Alloys*, Vol. 1, No. 17, 1930, p. 835.

[42]These words are used to denote either solid solution or a compound.

[43]The question discussed is that of molecular nitrogen: The introduction of nitrogen by means of ammonia is beside the point.

grees Fahr.) while in our work, and, previously by Adcock (42), the same purpose was accomplished by *remelting* chromium under nitrogen at atmospheric or reduced pressures.

A few preliminary alloys prepared in this manner contained approximately 10, 20, and 53 per cent chromium, the remainder being iron. Upon completion of the analysis for nitrogen, the percentage of the latter was plotted against chromium, as shown in Fig. 27,

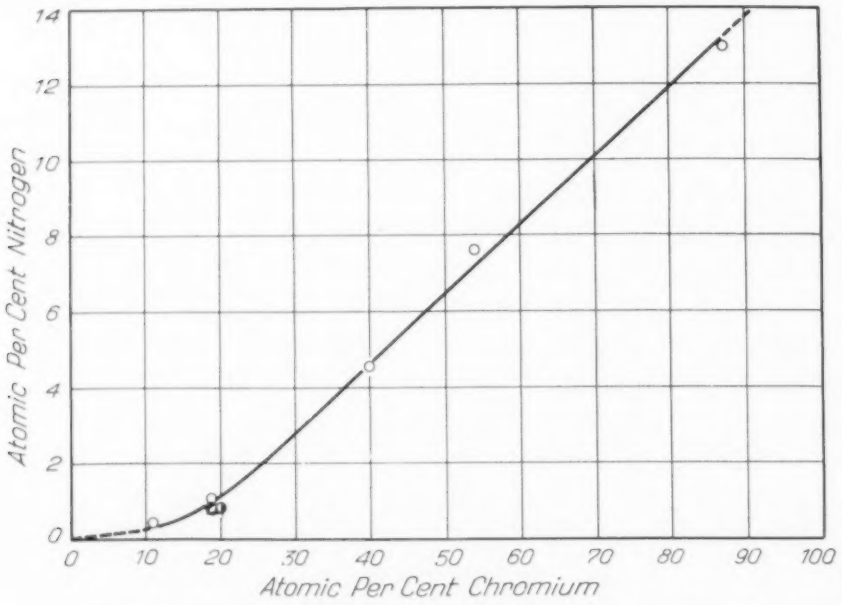

Fig. 27—Diagram Showing the Relationship Between Chromium and Nitrogen Contents of Iron-chromium-nitrogen Alloys.

incorporating in this curve results obtained by Adcock (42). It becomes evident at first glance that the amount of nitrogen absorbed during remelting is directly proportional to the chromium concentration, except for a slight deviation from the straight line when chromium is less than 10 per cent by weight.

To test this observation still further, a series of six alloys was prepared, using different raw materials and modifying experimental procedures. The charge, in each case, was calculated to have the same chromium content, but to vary widely in the content of nitrogen. The details of the melting charges, the calculated and the actual analysis are given in Table VII.

Regardless of the initial composition of the charge the final nitrogen percentage was the same, obviously determined by the chromium in the alloys. It may be arbitrarily called "maximum allowed." By changing the composition of the gaseous mixture, as was done

Table VII

Alloy No.	Experimental Conditions	Analysis, weight per cent Calculated Cr	Calculated N_2	Actual† Cr	Actual† N_2	Actual† C
N_2 bearing Fe-Cr	Fe-Cr and Frey iron remelted under 1 atmo. N_2.	55.4	nil	55.52	2.08	.021
18 N 1	N_2 bearing Fe-Cr (2.1% N_2), Fe-Cr and Frey Fe, remelted under atmos. pressure of N_2. Absorption of N_2 during melting noted.	17.9	.366* .197**	17.84	.207 .205	.014
18 N 2	N_2 bearing Fe-Cr, Fe-Cr, and Frey Fe, remelted in atmos. of N_2 and argon (partial pressure of N_2 0.27 atmos.).	17.8	.116**	18.26	.145	.008
18 N 3	N_2 bearing Fe-Cr and Frey Fe, melted under 1 atmos. of N_2. Evolution of N_2 on melting noted.	19.3	.730	19.06	.215 .209	.013
18 N 4	Fe-Cr and Frey Fe, melted under 1 atmos. of N_2. Absorption of N_2 during melting noted.	18.1	nil**	18.06	.213	.009
18 N 5	Fe-Cr and Frey Fe, melted under 1 atmos. of N_2. Absorption of N_2 during melting noted.	10.3	nil**	10.29	.121	.016
18 N 6	N_2 bearing Fe-Cr and Frey iron melted under 1 atmos. of N_2. (Check on alloy 18 N 3). Evolution of N_2 on melting noted.	18.3	.690	18.16	.211	.010

† When two figures for analysis are given they were secured by independent laboratories.

* Based on observed amount of N_2 used during melting (in addition to N_2 from N_2 bearing Fe-Cr).

** Based on N_2 in nitrogen in charge.

in the case of alloy 18 N 2, it is possible to control nitrogen concentration, i.e., to introduce less nitrogen than the "allowed maximum." But to increase under the described experimental procedure the concentration above the maximum was found impossible.

Realizing this unusual affinity of iron-chromium alloys for nitrogen, it appeared indeed desirable and important to ascertain the influence of nitrogen on the constitution and properties of the chromium alloys.[44] The available literature contains comparatively few and incomplete reports. Adcock, in his work already mentioned (42), alludes to the structural changes in chromium steels, brought about by the presence of nitrogen. Fairly high carbon contained in the described alloys rendered the interpretation of the results somewhat difficult. Comprehensive experimental work on a series of alloys practically free from carbon and otherwise quite pure was undertaken. Two of the alloys containing respectively 10 and 18 per cent chromium, and with corresponding maximum nitrogen concentration were subjected to intensive studies in order to discern their nature and learn their fundamental characteristics.

Dilatometric, microscopic and, to a limited extent, X-ray methods

[44]The possible influence of N_2 on properties of iron and steel suggested as early as 1889 by Tholander (34). This question has been debated, pro and con, ever since, and is, lately, again revived by Svetchnikoff (35).

were made use of in securing the desired data. I am afraid that your patience has already been taxed so that only a brief summary of results will be offered.

Dilatometric observations immediately disclosed a very pronounced influence of nitrogen on the phase relationship in nitrogen-bearing alloys. It will be remembered that alloys of 18 per cent chromium are characterized by continuous, smooth "length-temperature" curves on which the existence of gamma to alpha transformation will

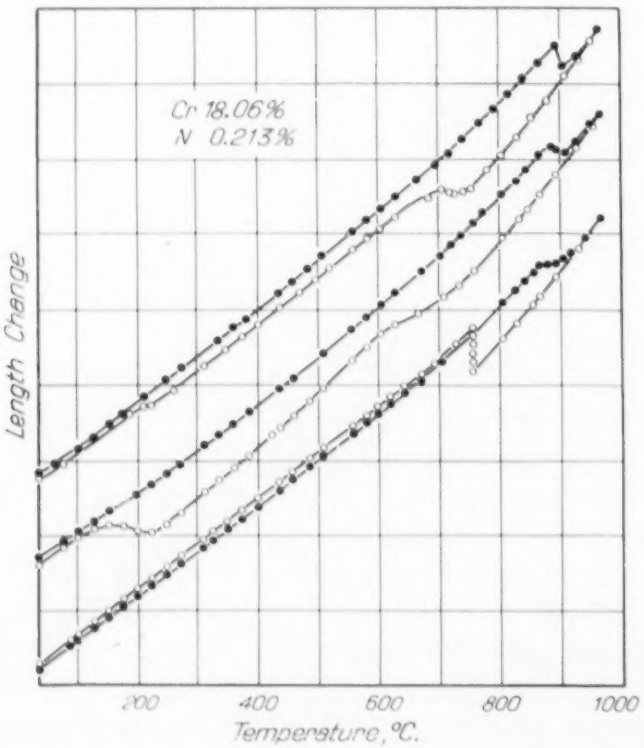

Fig. 28—Dilatometric Curves for Iron-chromium and Nitrogen Alloys.

be manifested only under special procedure for observations. The typical curve for the similar alloy but with nitrogen (Fig. 28) proves the existence of a definite, sharply defined transformation, both on heating and cooling. With smaller percentages of nitrogen the magnitude of the transformation diminishes, but the temperature range remains, apparently, unaffected. In other words, addition of nitrogen results in the formation, under equilibrium conditions, of increased amounts of the gamma phase, very much like carbon. In fact, nitrogen appears to be a more powerful factor than carbon. The volume change noted in nitrogen bearing alloy is definitely greater

than in the alloy with carbon in similar amount. This conclusion was fully substantiated later by microscopic observations. Similarly with carbon alloys, the transformation in nitrogen-containing alloys can be made to occur at any temperature between 200 and 800 degrees Cent. (390-1470 degrees Fahr.), depending on the rate of cooling. And, as should be expected, the common mechanical properties of the al-

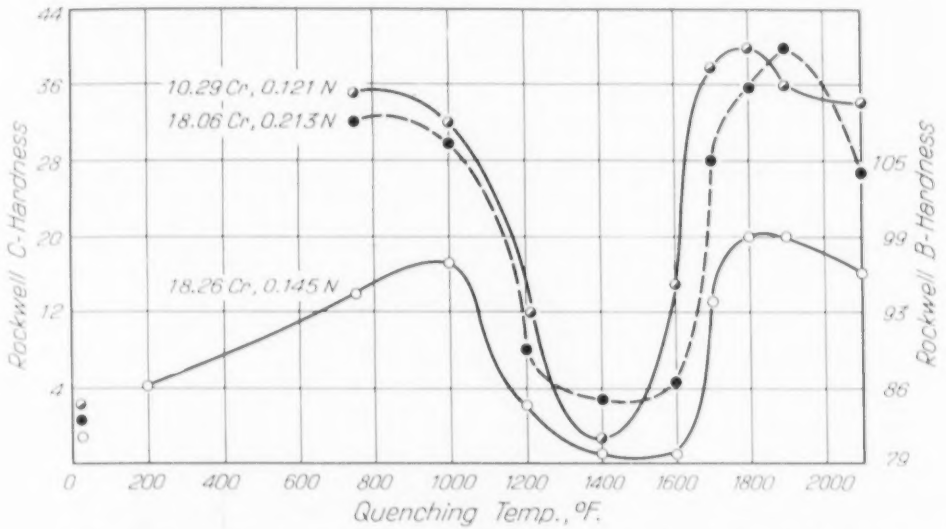

Fig. 29—Diagram Showing the Hardness of Iron-chromium-nitrogen Alloys after Quenching from Various Temperatures.

loys undergo radical changes when such alloys are subjected to the proper heat treatment.

As an example, the ability of the metal to harden is illustrated in Fig. 29, and should be compared with Fig. 30 for carbon alloys. It will be observed that the hardening power of nitrogen exceeds that of carbon.

The limited amount of material on hand precluded an exhaustive

Table VIII

Alloy Composition				
Chromium Per Cent	Nitrogen Per Cent	Carbon Per Cent	Treatment	Modified Charpy Foot-Pounds
17.84	0.207	0.01	Normalized from 1650°F.	3-4
			Annealed at 1400°F., air-cooled.	15.0
			Very carefully annealed, slowly cooled.	72.0
18.26	0.145	0.006	Normalized from 1650°F.	120.0
			Quenched in oil and drawn at 1400°F.	113.0
			Annealed at 1400°F., and air-cooled.	83.0

study of mechanical properties, although it was possible to determine impact toughness in two important alloys. By controlling the nitrogen content and with proper heat treatment, impact characteristic, far above those obtainable in alloys without nitrogen, can be easily se-

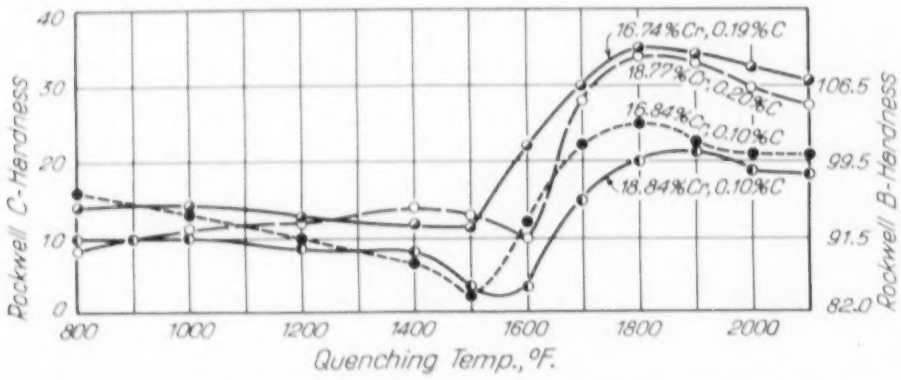

Fig. 30—Diagram Showing the Hardness of Iron-chromium-carbon Alloys after Quenching from Various Temperatures.

cured. An illustrative summary will be found in Table VIII.

The microscopic study of the constituents, their nature and their interrelation was found to be in complete agreement with the results previously obtained by other methods. The best way to describe it is by means of illustrations.

The alloys of iron-chromium and nitrogen appear to be built up of the following:

Equilibrium Phases:

(a) Ferrite—a solid solution of iron, chromium and probably some nitrogen.

(b) A compound the nature of which is as yet subject to speculation. Time at our disposal did not permit a thorough X-ray study. Preliminary results showed the lines only for alpha iron, with a_o apparently unaffected by nitrogen (a_o = 2.8675 for alloy with 0.21 per cent nitrogen and a_o = 2.8676 for the same alloy with nitrogen of 0.015 per cent). Although the efforts were made to ascertain whether, upon dilution with iron, the latter is substituted, in part for chromium, the results are too indefinite.[45]

(c) Austenite: At high temperatures the compound goes into solid solution with ferrite, forming austenite.

[45]Blix (44) reports another compound, hexagonal type, if nitrogen content exceeds 33 per cent. This phase is obviously non-existent in the alloys under discussion.

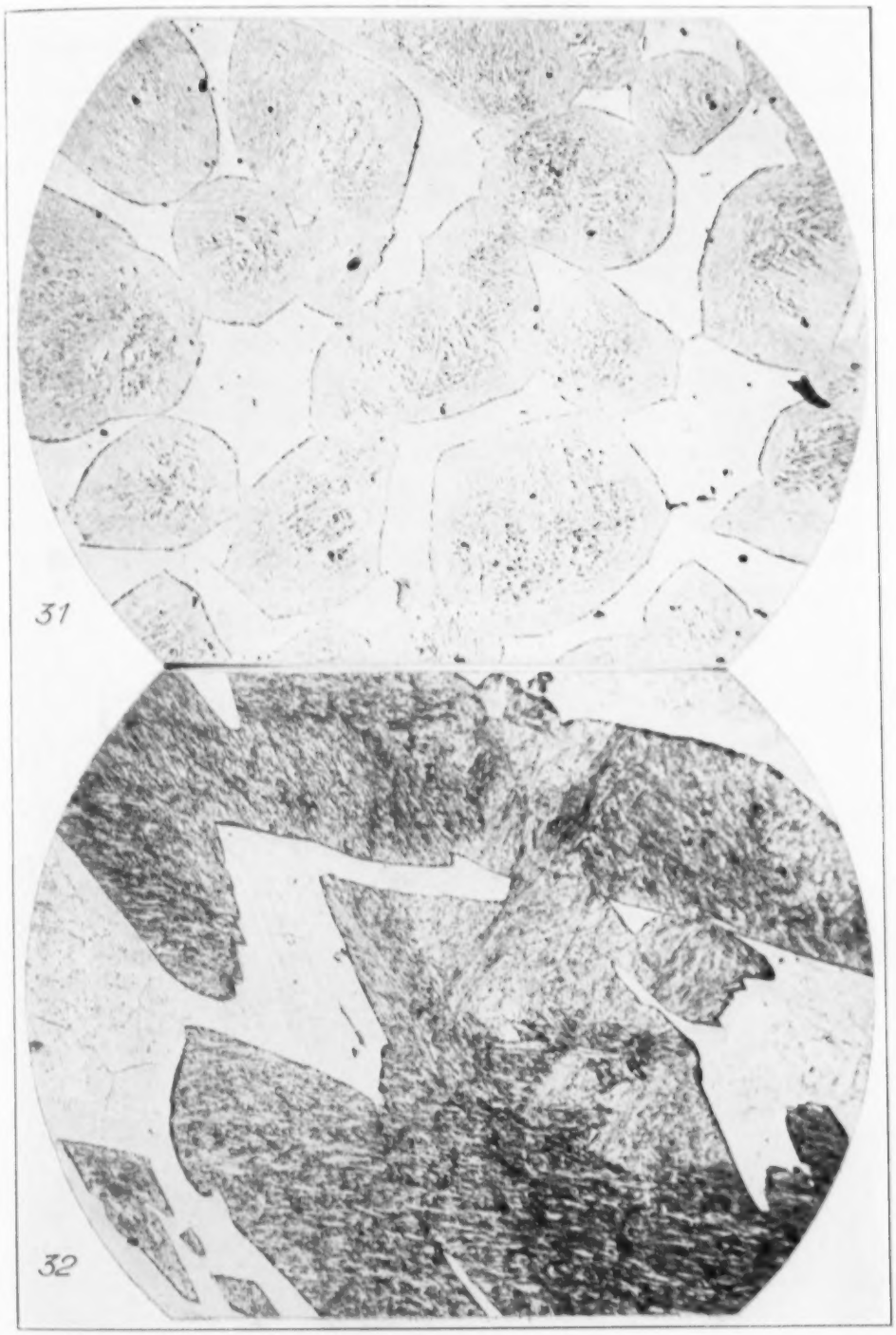

Fig. 31—Photomicrograph of the Structure of an Alloy Containing 18.1 Per Cent Chromium and 0.213 Per Cent Nitrogen. Homogenized for 12 Hours at 2250 Degrees Fahr. and Air-Cooled. × 120.

Fig. 32—Photomicrograph of Fig. 31 After Partial Decomposition Showing Typical Martensitic Appearance. × 230.

Structural Constituents:

(1) Martensite—a product of incomplete decomposition of austenite upon cooling: the word is used arbitrarily to denote the structural appearance of the constituent.

(2) Pearlite—an eutectoid of ferrite and compound, formed from austenite upon exceedingly slow cooling.

It was previously stated that nitrogen-bearing alloys exhibit greater volume change during the gamma-to-alpha transformation than alloys in which carbon is substituted for nitrogen in similar amount. This is upheld by Fig. 31 showing the structure of 18.1 per cent chromium, 0.213 per cent N_2 alloy, homogenized for 12 hours at 2250 degrees Fahr. (1230 degrees Cent.), and cooled in air. The relative amount of austenite in equilibrium with ferrite at the high temperature of treatment, is almost predominating. Naturally, at the rate of cooling used, the austenite has not been retained as such. Its partial decomposition presents typical martensitic appearance. (Fig. 32.)

The alterations in the nature of martensitic constituents, upon attempts to bring it closer to equilibrium do not deviate from the usual process as we know it in ordinary steels. Heating the alloys to 900 degrees Cent. (1650 degrees Fahr.) for a sufficiently long time (1700 degrees Fahr (925 degrees Cent.) is below critical range) results in separation and agglomeration of the compound as will be seen from Fig. 33 (17.8 per cent chromium, 0.145 per cent N_2), and from Fig. 34 (18.1 per cent chromium, 0.213 per cent N_2).

In this structural condition, alloys possess maximum softness and ductility.[46] The phases at equilibrium within the three-phase region can be seen in Fig. 35. Holding within this region and regulated, slow cooling resulted in the formation of typical pearlite, compound, and ferrite.

At the temperature of 1000 degrees Cent. (1830 degrees Fahr.), the three-phase region is passed and alloys are composed of austenite and ferrite. The success in retaining austenite depends entirely on the rate of cooling. In Fig. 37 is illustrated the structure of the alloy with 17.8 per cent chromium and 0.145 per cent nitrogen after holding at 1000 degrees Cent. (1830 degrees Fahr.) for three hours and very rapid cooling in ice brine. The grains of austenite are dispersed through the matrix of ferrite.

[46]Deeper etching of the samples would result in the pitting of ferrite, masking its appearance. It is probable that this "pitting" is in reality etching around small particles of compound separated from ferrite (Fig. 36).

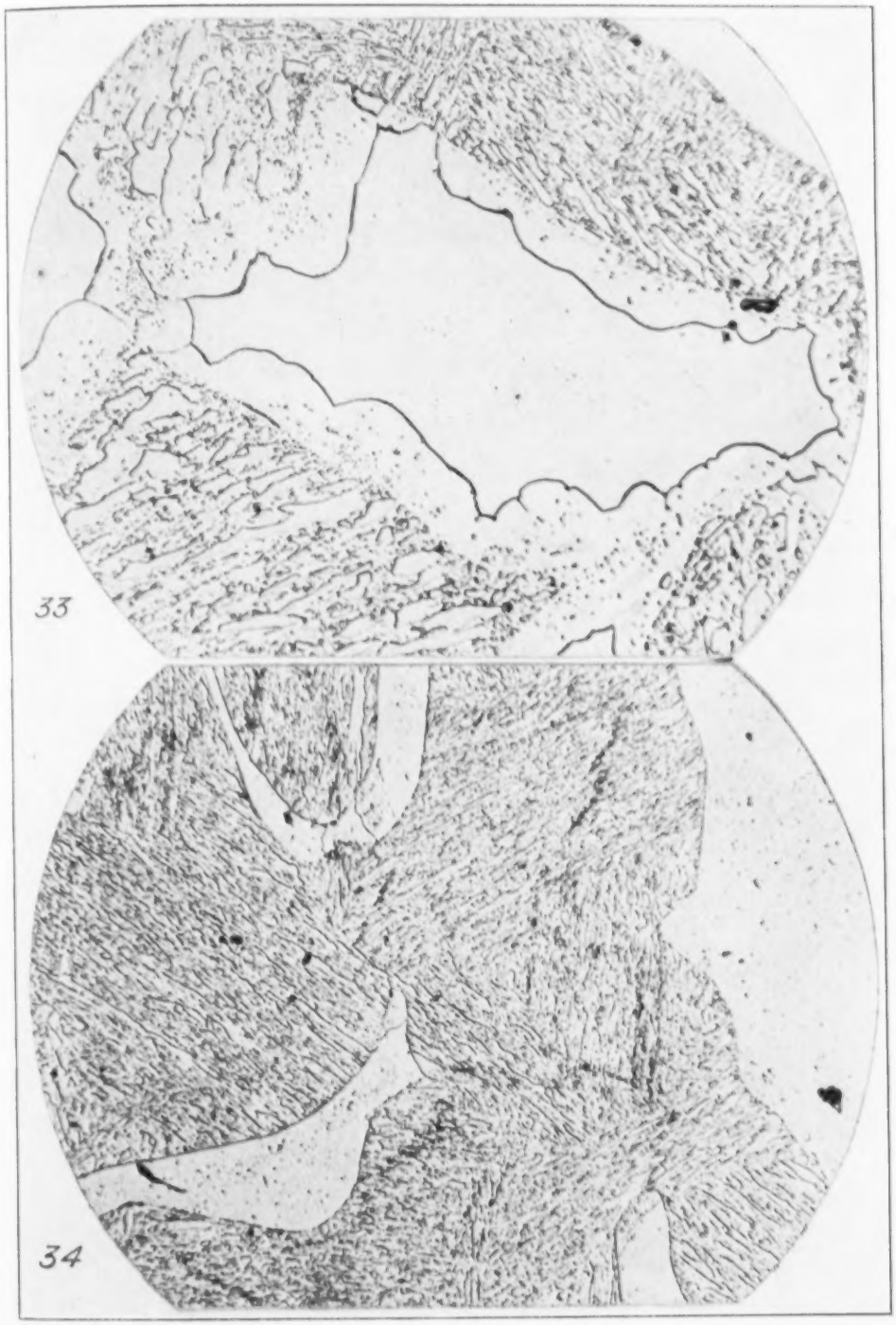

Fig. 33—Photomicrograph of the Structure of an Alloy Containg 17.8 Per Cent Chromium and 0.145 Per Cent Nitrogen After Heating to 1700 Degrees Fahr. and Quenching, Showing Agglomeration. × 530.

Fig. 34—Photomicrograph of the Structure of an Alloy Containing 18.1 Per Cent Chromium and 0.213 Per Cent Nitrogen After Heating to 1700 Degrees Fahr. and Quenching. × 530.

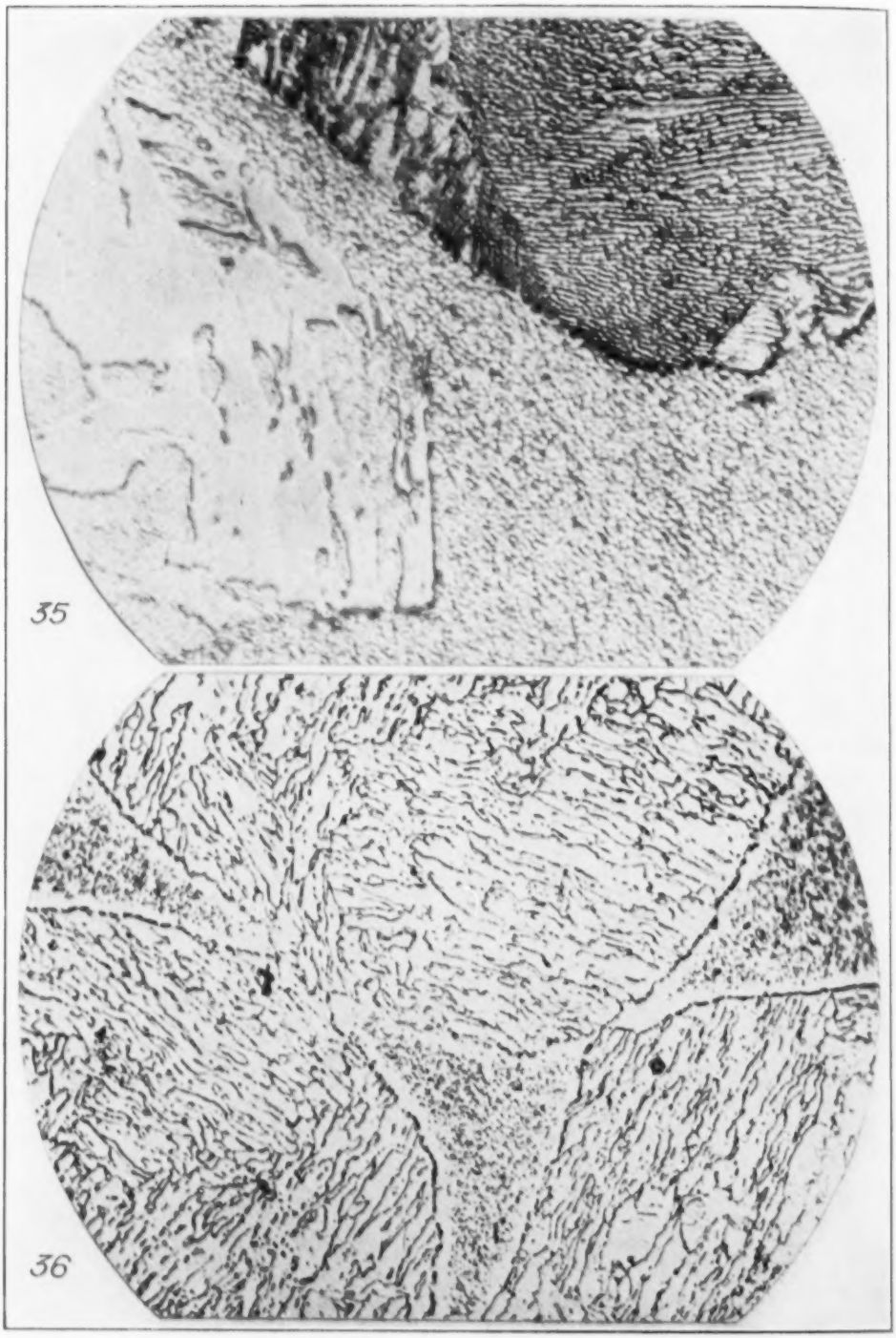

Fig. 35—Photomicrograph Showing the Phases at Equilibrium Within the Three-Phase Region of an Alloy Similar to Fig. 34. Annealed at 1220 Degrees Cent. × 1760.
Fig. 36—Same Annealed at 1600 Degrees Fahr. Showing Typical Pearlite and Ferrite. × 500.

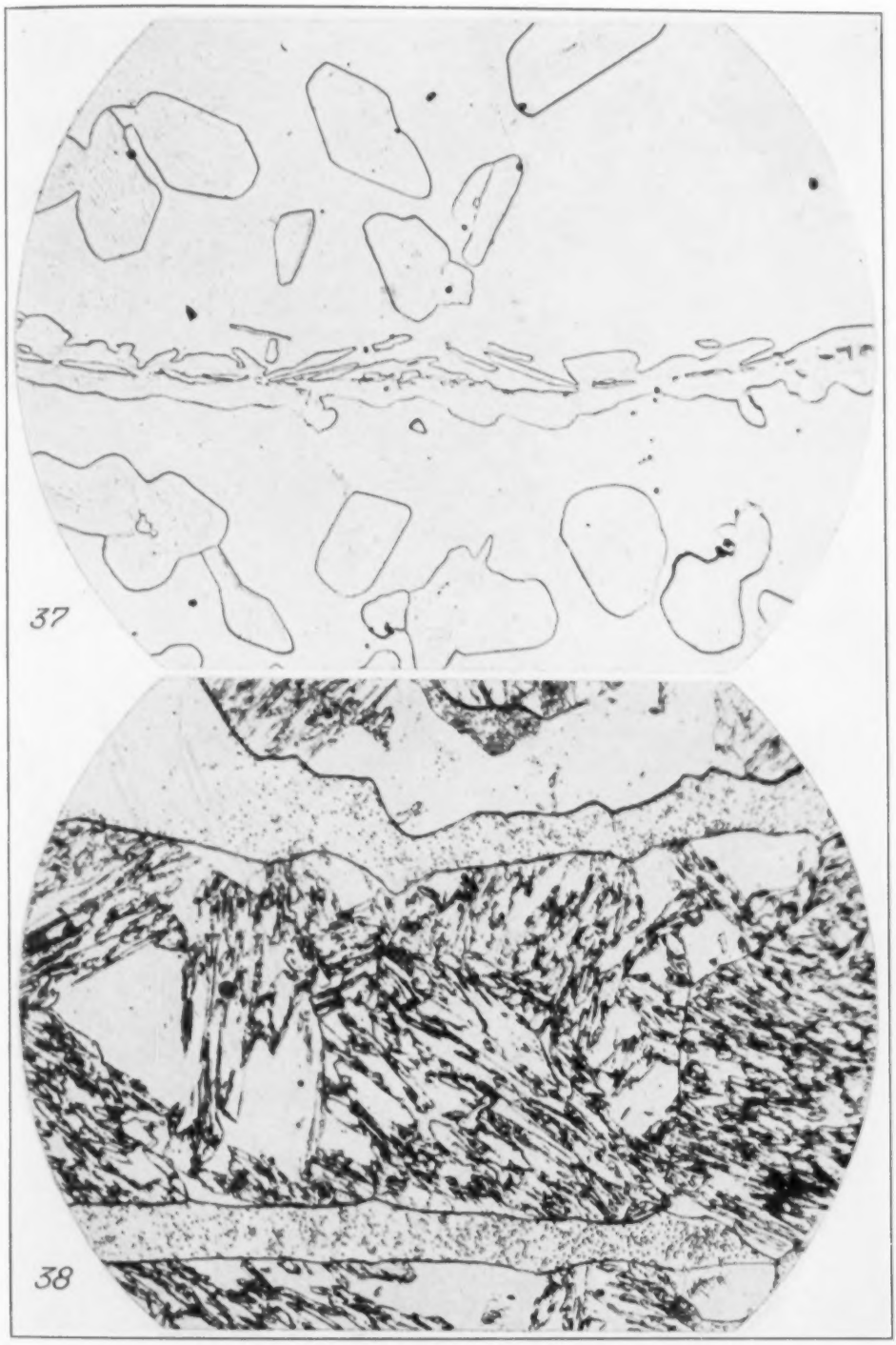

Fig. 37—Photomicrograph of an Alloy Containing 17.8 Per Cent Chromium and 0.145 Per Cent Nitrogen Quenched from 1800 Degrees Fahr. in Brine. × 100.

Fig. 38—Photomicrograph of an Alloy Containing 18.1 Per Cent Chromium and 0.213 Per Cent Nitrogen Less Rapidly Quenched from 1800 Degrees Fahr. × 530.

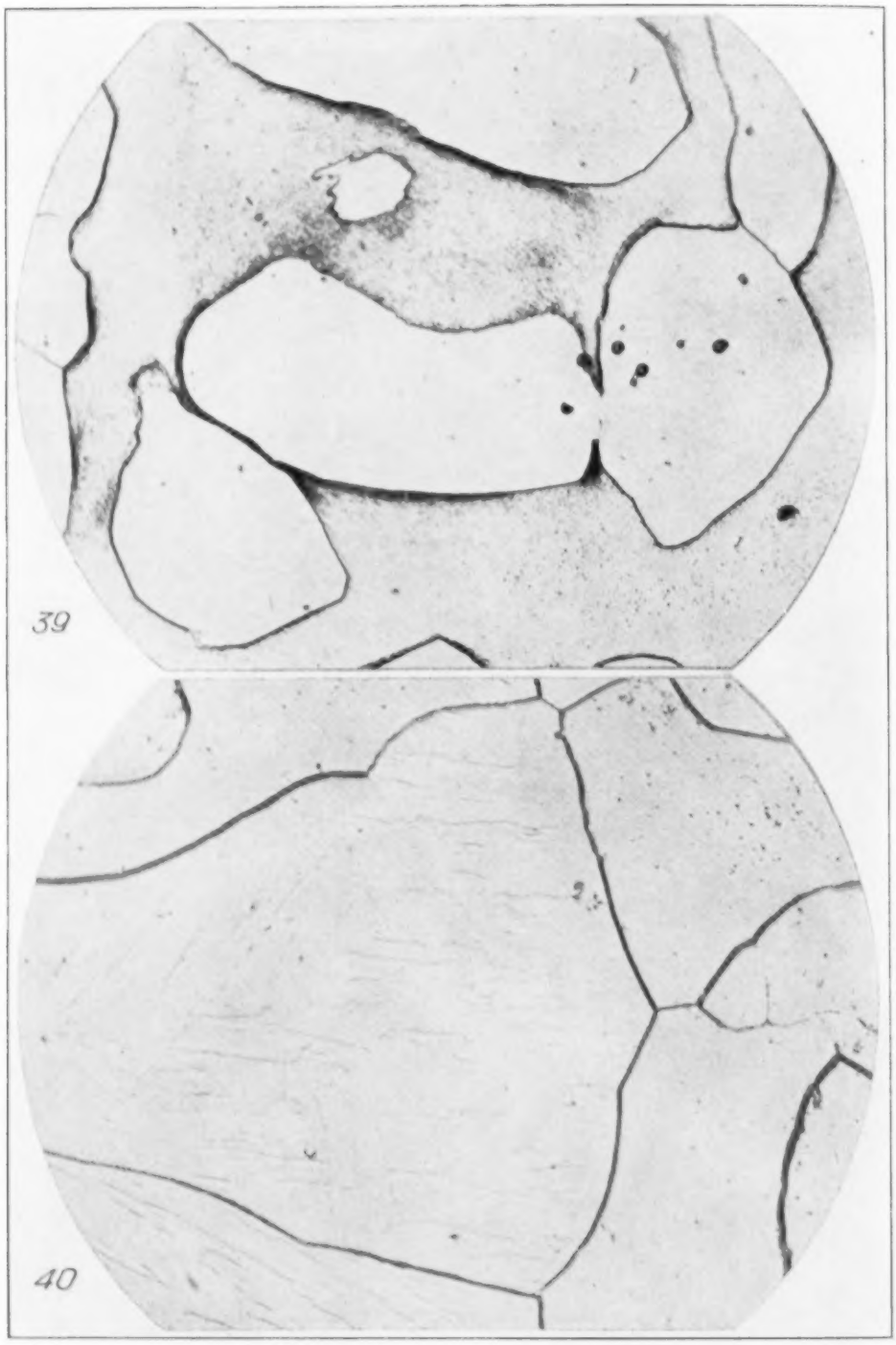

Fig. 39—Photomicrograph of Chromium Alloy Containing 0.145 Per Cent Nitrogen Quenched from 1900 Degrees Fahr. × 530.
Fig. 40—Photomicrograph Similar to Fig. 39. × 1000.

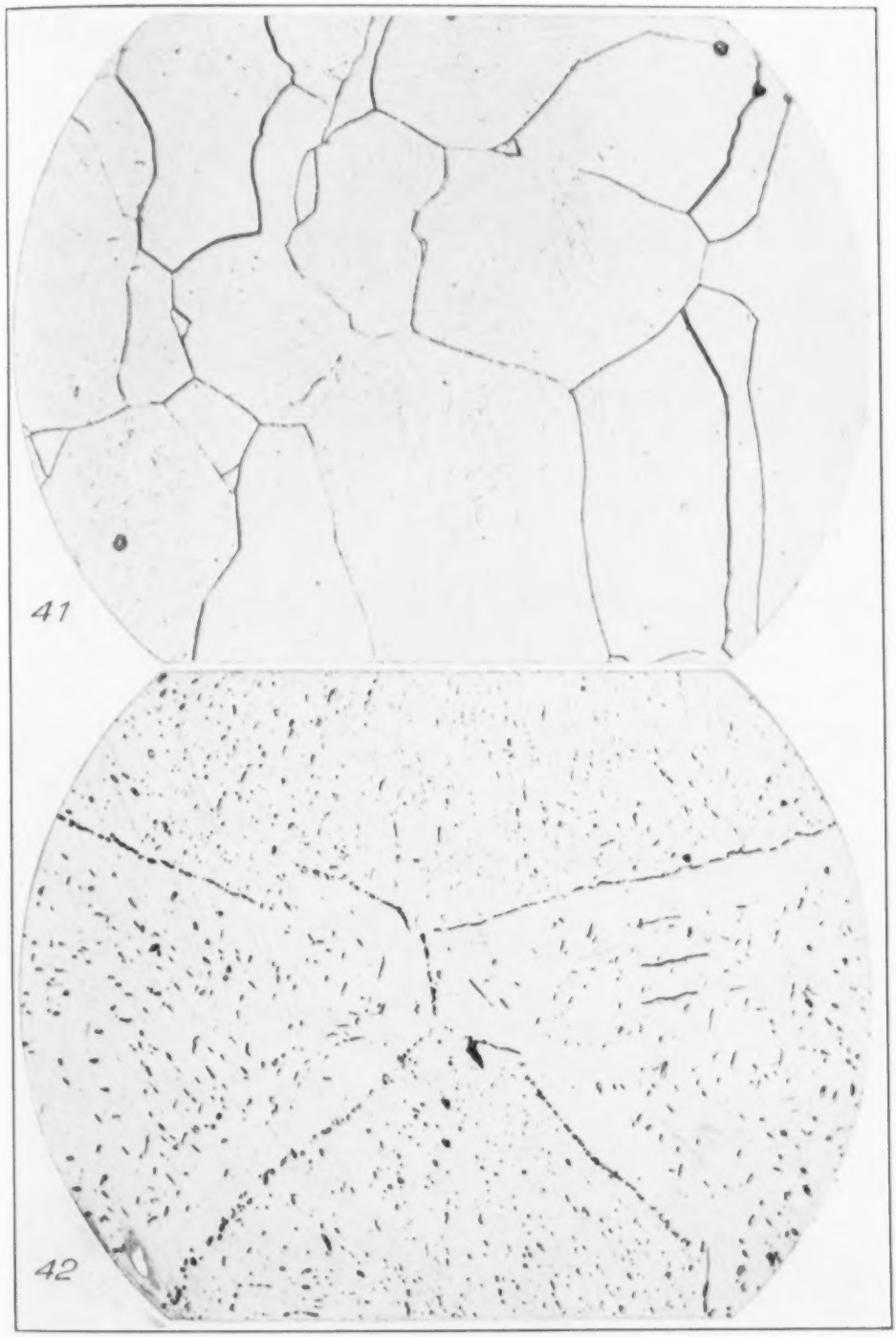

Fig. 41—Photomicrograph of Chromium Alloy Containing 0.213 Per Cent Nitrogen Quenched from 1900 Degrees Fahr. Appears to Enter the Field of a Single Gamma Phase. × 530.

Fig. 42—Photomicrograph of Alloy Annealed from 1700 Degrees Fahr. Showing a Structure Resembling Nitrogen Needles. × 500.

Fig. 43—Photomicrograph of Alloy Same as Fig. 42 Annealed from 1700 Degrees Fahr. Showing a Structure Resembling Nitrogen Needles. × 2250.
Fig. 44—Same as Fig. 43 at High Magnification Showing Shattered Appearance of Needles. × 2250.

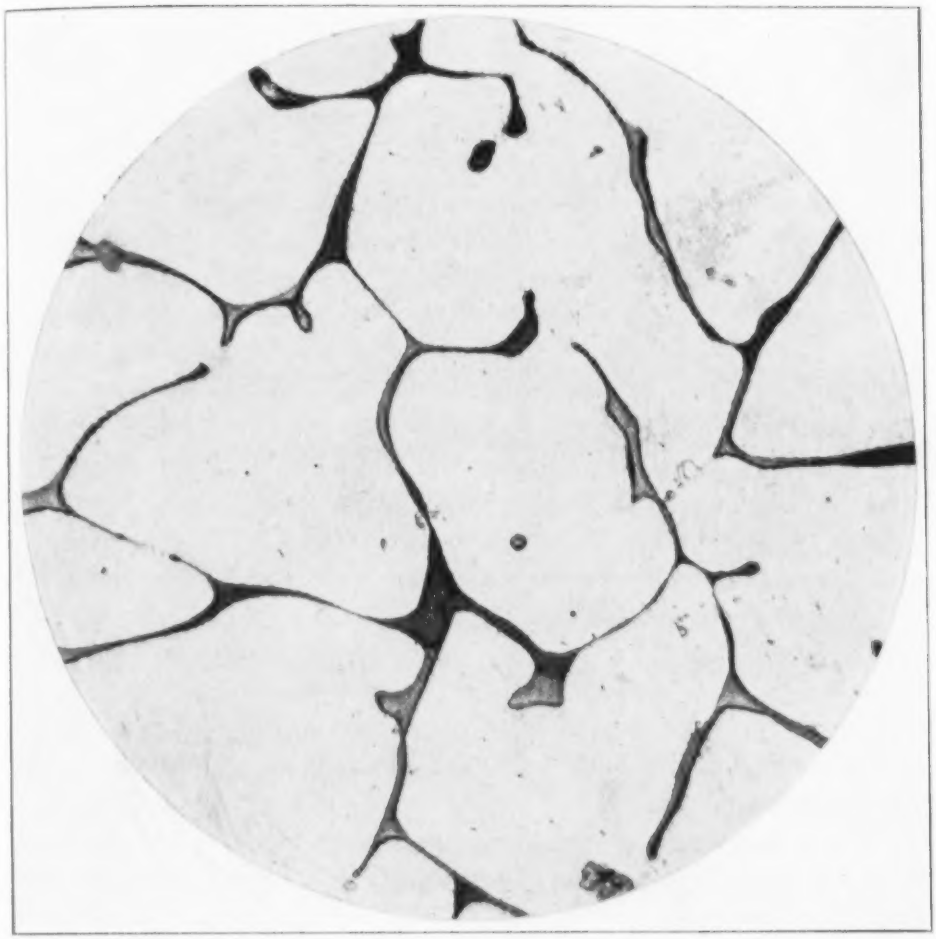

Fig. 45—Photomicrograph of Chromium Alloy Containing 10 Per Cent Chromium Showed Markedly Less Resistance to Corrosion. Quenched from 750 Degrees Fahr. × 230.

Alloy with 18.1 per cent chromium and 0.213 per cent nitrogen (Fig. 38) less rapidly quenched shows a presence of typical martensite, predominating over ferrite because of higher concentration of nitrogen.

At increasingly higher temperatures the alloy with 0.145 per cent nitrogen does not undergo any further change. Even just below the melting point, both ferrite and austenite are still present, easily distinguished by their typical appearance. These structures are illustrated in Figs. 39 and 40.

Upon increasing temperature the alloy with 0.213 per cent nitrogen appears to enter the field of a single gamma phase. At 1200 degrees Cent. (2190 degrees Fahr.) and above, only very small and

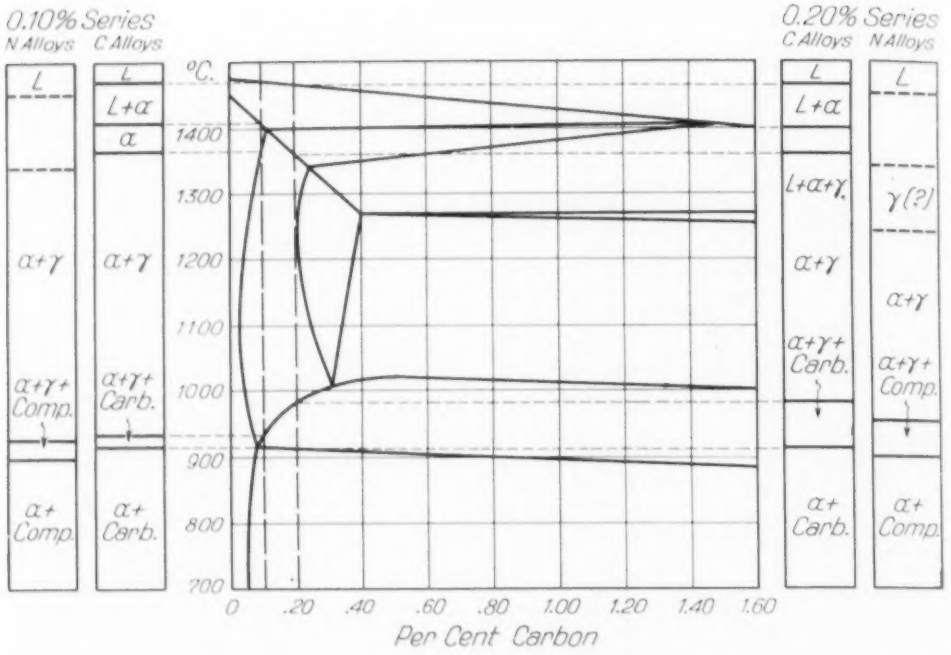

Fig. 46—A Schematic Diagram for Alloys of Iron, 18 Per Cent Chromium, and Carbon; also for Alloys of Iron, 18 Per Cent Chromium, and Nitrogen.

isolated ferritic grains could be found (Fig. 41)—which may not be a true equilibrium phase.

When separation of the compound takes place at temperatures below the three-phase region it sometimes takes on a peculiar form of platelets, somewhat resembling well-known nitrogen needles (Figs. 42 and 43). The dark appearance of these plates is due to staining.

It also appears that the compound is quite brittle from its shattered appearance at high magnification (Fig. 44).

The same structural constituents were also found in alloys of other compositions, the amounts of various phases being of course dependent upon analysis. Alloys of lower chromium, 10 per cent or less, were observed to have markedly lower resistance to corrosion. Even upon etching with dilute acids the ferrite constituent is deeply stained. Its typical appearance can be seen in Fig. 45.

The experimental facts presented for your consideration reveal a striking analogy in the "build up" of alloys with carbon or nitrogen. The study as a whole, however, should be accepted as qualitative. The derived information is not sufficient to present a structural diagram for iron-chromium-nitrogen system, much less an equilibrium diagram. The powerful influence of nitrogen on practically carbon-

less chromium-iron alloys can nevertheless be represented by a schematic diagram reproduced in Fig. 46.

For its construction, alloys of the same chromium percentage were selected, namely 18 per cent, but containing either carbon or nitrogen, in *equal* amounts. Vertical isotherms, corresponding to a given carbon concentration, were drawn until they intersect the limits of various fields and are then projected on the column to the right of the diagram. The regions occupied by various phases and their temperature limits become clearly represented. Side by side is shown an analogous representation of experimental data for nitrogen-bearing alloys. Of course, these simplified graphs do not convey the idea of the relative amounts of different phases. From the examination of numerous structures and heat treatment data, it would appear that the eutectoid composition corresponds to much lower values of nitrogen than of carbon. In fact, it is quite definitely reflected in some of the mechanical properties of the alloys.

The discussion of nitrogen in iron-chromium alloys was deliberately confined to alloys with very little or no carbon. What influence nitrogen may have on chromium irons and chromium steels, or, for that matter, on other highly special alloys can, at the present stage of our knowledge, only be speculated upon. For this reason it had better be left undiscussed.

The complex nature of iron alloys can be understood only through fundamental research that finds and analyzes basic facts.

I have presented to you the studies which have uncovered many involved phenomena in alloys of iron with chromium. As I attempted to show, the same phenomena are existent in other alloy systems.

Should you judge that the studies presented deserve the title "fundamental," I would want to hope that Professor Edward De Mille Campbell, who was a leader in such work, would have considered as fulfilled the purpose of the Lecture in his honor.

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To Albert Sauveur who has inspired me to work in the field of metals, I express my deep gratitude.

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And finally, with a deep sense of appreciation, I wish to thank the Trustees of the American Society for Metals for the honor they have conferred upon me.

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STUDIES ON THE METALLURGY OF ARC DEPOSITED WELD METAL

By Samuel L. Hoyt

Abstract

The author describes weld metal as deposited with the cellulose type of weld rod, including chemical analysis, mechanical properties, and structure. The same features of weld metal deposited with the bare wire electrode are also given for comparison. In particular the occurrence of oxygen as FeO, MnO, SiO_2, and Al_2O_3 is given for different weld metal types as determined by the "fractional oxygen" method of analysis, while the significance of foreign inclusions is treated in some detail. These results are shown to characterize the metal metallurgically as is shown by the results of tests for normality, hot shortness, strain and quench aging, etc.

DISCUSSIONS on welding have assumed an important place in the technical literature, and justifiably so on account of the status which the art of welding has attained in the past decade. In a very true sense this art is metallurgical in nature because its success depends upon a proper control of effects which govern metal quality while limitations are imposed by the degree of control thus exercised. This is particularly true of metallic arc welding which involves the melting, solidification, and subsequent heat treatment of the metal in and adjacent to the weld seam. The actual technique employed, including weld rod, is responsible for weld metal quality and, to use extreme though real cases, it may give variations from oxidized and dirty metal to clean and sound metal of the best quality. Thus the importance of the process and its inherent metallurgical characteristics justify serious attention on the part of the metallurgist. In the present discussion it will be this phase of arc welding which will receive attention and particularly the so-called "modern" methods of welding.

While the author wishes to limit himself to his own definition of modern arc welding, he presumes that the term is generally used to mean welding with cellulose-covered weld rods, or with weld rods

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which derive their important characteristics from cellulose coatings. This type of welding has been pioneered over the past sixteen years by the company with which the author is associated and originated with the paper-covered welding rod developed by R. S. Smith, then chief engineer of the A. O. Smith Corp. This occurred in connection with a large contract for aerial bombs during the late war. The important features brought out by that experience were ability to manufacture bombs whose welded joints withstood the severest service and acceptance tests, and a proper adaptation of welding rods and welded product to routine commercial production. Since that time, covered welding rods of this type have been extensively used in the welding of a large variety of products subjected to extremely severe operating conditions.

Much of the information used here was gained in a study made on welds in 1-inch plate stock. Various types of welding rods were used, including bare wire and cellulose coated welding rods, and in each instance the technique of welding was correct for the welding rod used. Welding rods with a slag or flux coating were also studied and some reference will also be made to the characteristics of the weld metal made with them. After the test plates were welded together and given a stress-relieving treatment at 1200 degrees Fahr., sections were machined from the block and studied by physical, chemical and metallurgical tests. The welding was all done under the supervision of L. J. Larson and the physical tests under T. M. Jasper, both of the Research and Engineering Department. The metallurgical tests were made on cross sections through the weld and the plate stock, which is made clear from the photomacrographs discussed later, though some of the tests required somewhat larger test pieces. Actually these tests were conducted in about the usual way for welds and the procedure need not be described in detail. In some cases the tests represent "all weld metal." Such test pieces can easily be secured from welds made in 1-inch plates by simple machine shop operations, at times using a light macro-etch to outline the weld proper.

Weld Metal Made With Bare Wire Electrodes

When the bare wire electrode is used, no provision is made to protect the metal during deposition, consequently the metal melts and solidifies while directly exposed to the air. This condition is

favorable to the absorption of oxygen and nitrogen and is aggravated by the action of the arc in ionizing those gases or in converting them from their normal molecular state to the atomic state. With these conditions in mind the metallurgical considerations suggest that the chemical analysis of the weld metal will show copious quantities of oxygen and nitrogen, and it may likewise be expected that the carbon and manganese will be low. Such observations have been made frequently in the past and have been reported in the literature by other investigators.[1] A representative analysis of bare wire weld metal is as follows:

	Per Cent
Carbon	0.05 and less
Manganese	0.10 and less
Silicon	0.01
Phosphorus	0.02
Sulphur	0.03
Oxygen (total)	0.20 and more
Nitrogen	0.15

Of the elements reported, oxygen and nitrogen are seen to be the principal constituents of bare wire weld metal. The first five elements are those commonly determined in steel and they, taken by themselves, suggest that this metal is relatively soft and ductile; yet in another sense this is an off composition because this is a cast metal and the carbon, manganese and silicon are too low and the sulphur is too high for the manganese. Not only is this ratio of manganese and sulphur bad but it is particularly bad in the presence of such a large amount of oxygen. We may expect this weld metal to be lacking in toughness and ductility at room temperature.

The physical properties of bare wire weld metal from welds in 0.25-inch plates are about as shown in the following tabulation:

Yield point	35,000 to 40,000 pounds per square inch
Tensile strength	50,000 to 60,000 pounds per square inch
Elongation, 2 inches	6 to 12 per cent
Reduction of area	8 to 20 per cent
Brinell Hardness number	100 to 110

These values were determined from tests on welds made on 0.25-inch plates and agree well with the values reported in the literature by other investigators.[2]

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[1]See H. S. Rawdon, E. C. Grosbeck and L. Jordan. Technological Paper, U. S. Bureau of Standards, No. 179, Nov. 15, 1920.

[2]The Bureau of Standards report (Loc. cit.) gives figures for a "good weld" in 0.25-inch plate of 60,610 pounds per square inch tensile strength and 5.5 per cent elongation in 6 inches, for example.

The elongation and reduction in area for bare wire welds made on 1-inch plates are generally lower than for welds in 0.25-inch plates, although the maximum values obtained approach the upper limits given in the preceding table. The ultimate strength for welds in 1-inch plates is some 5,000 to 20,000 pounds per square inch lower than the upper limit of strength given for welds in 0.25-inch plates. The Charpy values obtained on specimens of bare wire weld metal taken from welds in 1-inch plates are from 1 to 2 foot-pounds, with the standard key hole notch with a radius of 1 millimeter in the 1-centimeter square bar.

The weld metal is stronger than would be expected with such low carbon, while the ductility and toughness are lower than would be indicated by the low carbon content. The relatively high strength is a valuable quality but the low ductility seriously impairs the usefulness of these welds. Reasons for this deficiency will be given later but whatever the cause may be, the high oxygen and nitrogen contents are inconsistent with metal of high quality. Even so, it is not possible to correlate the brittleness directly with the analysis because the factors of porosity, dirt, and shrinkage cracks also contribute their own effects.

The oxygen content as reported in Table I was that determined by the usual method of vacuum fusion which gives the "total oxygen" content. A more accurate index of metal quality is given by the "fractional oxygen" method developed by Dr. L. Reeve and which has been described by him in a previous contribution.[3] This method reports separately the amounts of oxygen which are combined with iron, manganese, silicon and aluminum respectively. Fractional oxygen determinations on bare wire weld metal show that practically all of the "total oxygen" occurs as iron oxide, with a small additional amount as alumina. A typical analysis will be given subsequently in a comparison of this weld metal with that deposited with the cellulose-covered welding rod. The conclusion that we may tentatively draw here is that bare wire weld metal is "oxidized" metal, i.e., it contains large amounts of oxygen as iron oxide without adequate compensation. Our results on other types of "oxidized" iron or steel show that they likewise contain large amounts of iron oxide.

Coming to the structure of bare wire weld metal, these studies were made on 0.25-inch thick slices cut transversely through the

[3] L. Reeve, Iron and Steel Division, American Institute of Mining and Metallurgical Engineers; Contribution No. 56, July, 1933.

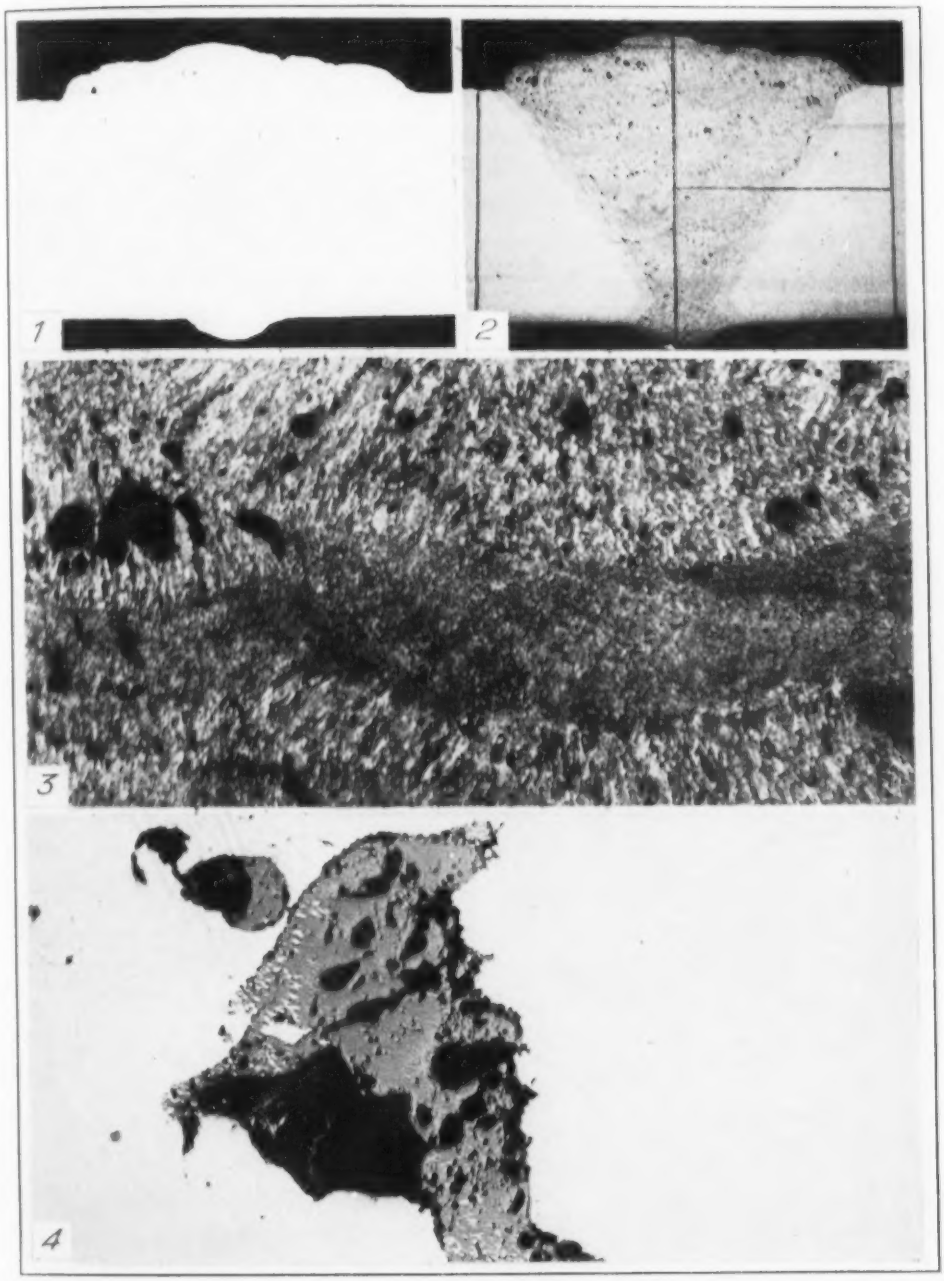

Fig. 1—Cross Section of Bare Wire Weld in 1-Inch Plate, As-Polished. × 1.
Fig. 2—Same as Fig. 1. Etched. × 1.
Fig. 3—Same as Fig. 2. × 9.
Fig. 4—Massive FeO Inclusion in Bare Wire Weld. × 100.

weld and plate stock as shown in Fig. 1. This is the full size polished cross section of the sample. The weld metal appears reasonably sound and clean and one would not expect this metal necessarily to

show a marked lack of metallurgical quality. The same section is shown in Fig. 2 after etching. This view shows the typical beads of the weld deposit which come from the deposition of successive passes and the heat effects caused thereby. The characteristics of the structure of the weld metal proper are shown in Figs. 3 and 4.

Descriptions of bare wire welds, which have appeared in the literature,[4] have indicated that pellets of oxidized iron become entrapped in the pool of metal under the arc and characteristic photographs have been given to illustrate the effect. This same occurrence was noted in the present study and were at first identified as these "oxidized pellets." It was found, however, that when the center of the spot was probed, a thin skin of metal came off to expose a small cavity below. This happened in every case. Therefore the theory of the inclusion of such pellets of metal is not valid. After a polished surface of bare wire weld metal has been cleaned up as described it presents a more porous appearance, but still on a fine scale.

An enlarged picture of bare wire weld metal is given in Fig. 3 which shows a typical field at higher magnification. Even here the major deficiency of the deposit which is shown, is porosity. By increasing the magnification to 100 diameters massive inclusions of iron oxide become readily visible, as in Fig. 4. These occur with such regularity that they may be considered to be inevitable in a process of depositing metal by droplets when exposed to a powerful oxidizing action. Some additional inclusions can be seen on the polished surface at 100 diameters of magnification but to gain the correct view of them it is necessary to make use of a lens with a higher resolving power. Such a photomicrograph is shown in Fig. 5 which reveals the fine dispersion of FeO throughout the deposit. This field also shows a few cracks which are believed to be due to shrinkage of the weld metal when at the hot short temperature range. While the FeO dispersion is uniformly distributed in the weld metal, the shrinkage cracks referred to are more or less isolated occurrences in the sections examined. Cracks of this character have never been observed in weld metal that was not hot short. This fine dispersion of globular iron oxide inclusions is typical of that constituent and we are inclined to the belief that these particles were dissolved in the molten metal and that they came out of solution upon solidification.

Upon etching the weld deposit it is seen that some portions are

[4]H. S. Rawdon, E. C. Grosbeck and L. Jordan, Loc. cit.

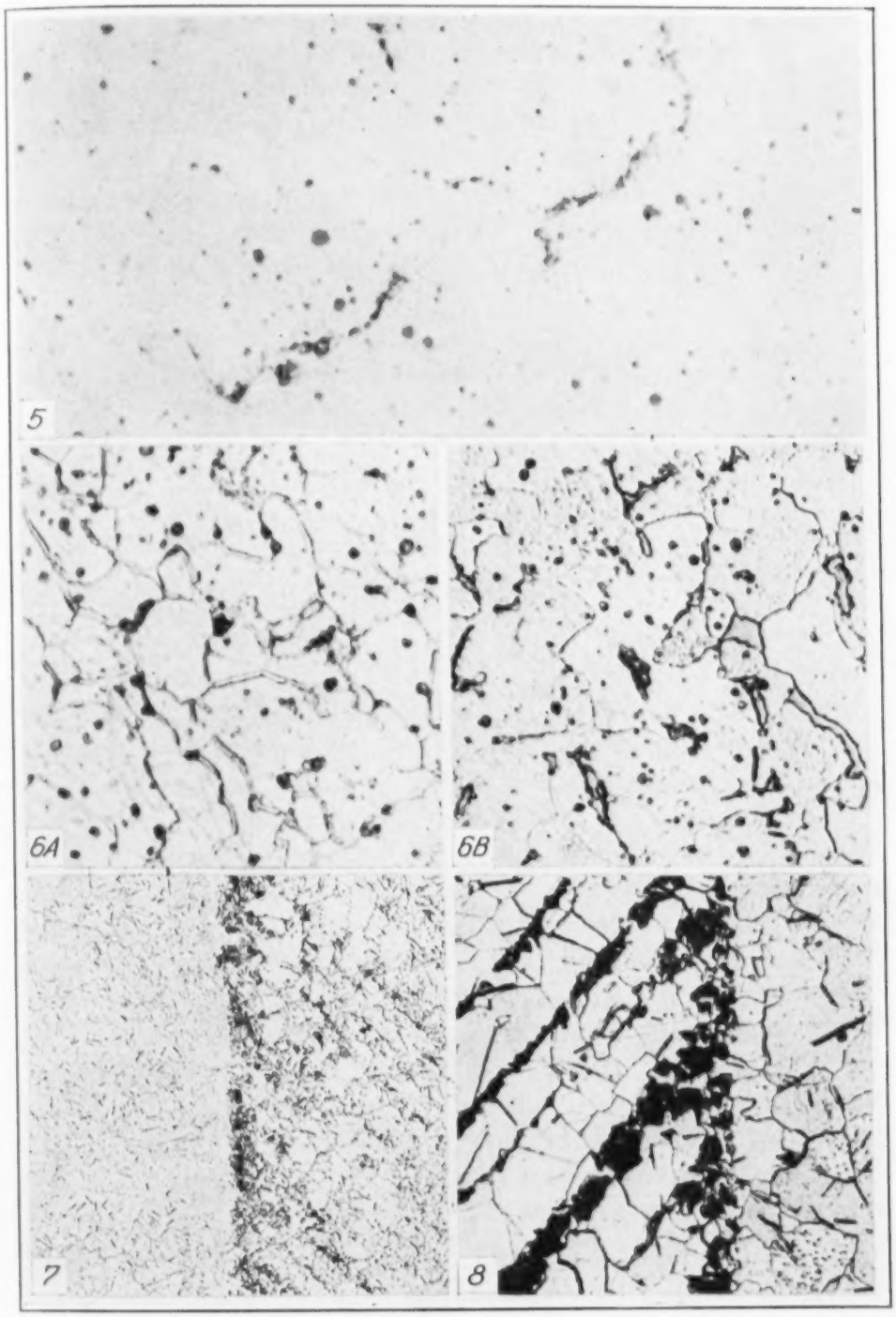

Fig. 5—Fine FeO Dispersion and Shrinkage Cracks in Bare Wire Weld. × 1000.
Fig. 6—Bare Wire Weld; Etched with 2 Per Cent Nital. × 1000.
Fig. 7—Junction of Bare Wire Weld and Plate in the As-Welded Condition after Reheating to 1200 Degrees Fahr. Etched with Nital. × 100.
Fig. 8—Same as Fig. 7, After Annealing at 1700 Degrees Fahr. Etched with Nital. × 200.

fine-grained (see Fig. 6) some are coarser-grained though still relatively fine-grained, and that others show a columnar crystallization. The nitrogen and, to some extent, the carbon produce a "pearlite-like" structure. Most of this is due to the nitrogen and is better shown after the sample is annealed. By means of a weak cupric reagent suggested by Comstock[5] we have been able to show that this "pearlitic" constituent in the weld metal etches dark before the pearlite of the plate stock is noticeably attacked, and we consider it to be braunite.

It is characteristic of the bare wire weld that a relatively sharp line of demarcation occurs between weld and the affected plate stock.[6] Fig. 7 shows the junction before annealing and Fig. 8 after annealing. The carbide segregation and nitride needles are readily observed. The latter occur even in the unfused portion of the plate stock showing that a nitriding effect has taken place.

Weld Metal Made With Slag or Flux-Coated Welding Rods

It would be going too far afield to attempt descriptions of welds made with the various coated weld rods of this type. The purpose of the coating seems to be to protect the weld metal while it is molten and during solidification, somewhat as molten steel is protected by slag. This applies specifically to the earlier welding rods of this type. The weld metal deposited by some of these welding rods was as strong as bare wire weld metal and was more ductile, though the total oxygen content was abnormally high for good metal. We believe that the small amount of silica which is present in this metal has a noticeably beneficial effect in improving its quality. The structure is similar to that shown in the photomacrographs for bare wire welds and it also appears here that the inclusion of massive slag inclusions is inevitable. In some instances at least, the nitrogen content is considerably less than that of bare wire weld metal. Taken in connection with the high iron oxide content, this must mean that while the slag has protected against the obsorption of atmospheric nitrogen, it has itself oxidized the weld metal.

Weld Metal Made With Cellulose-Covered Welding Rods

The cellulose-covered welding rod has a coating which is so

[5]G. F. Comstock, *Transactions*, American Institute of Mining and Metallurgical Engineers, 1922, Vol. 67, p. 306.

[6]W. E. Ruder, *Journal*, Franklin Institute, Nov. 1921, p. 561.

constituted that pyrolytic decomposition of the cellulose produces a powerful reducing gas at the arc, whose principal ingredients are hydrogen and carbon monoxide. Thus these welding rods are producers of reducing gases, in addition to such slags that are involved in their use. These gases eliminate the effects of the air and maintain a reducing condition for the transport of material from the welding rod to the plate and during the solidification of the deposited metal. The character and quality of the weld metal deposited under such favorable conditions are readily disclosed by a careful metallurgical examination.

A characteristic chemical composition of weld metal deposited by a cellulose-covered welding rod is given in the following tabulation:

	Per Cent
Carbon	0.08
Manganese	0.50
Silicon	0.20
Phosphorus	0.015
Sulphur	0.025
Oxygen (total)	0.06
Nitrogen	0.010

The carbon is somewhat higher than in the bare wire welds and is not far below that of the original welding rod. It seems likely that the well known decarburizing effect of hydrogen at elevated temperatures is in part responsible for the drop in carbon content. The manganese content is about the same as that of the welding rod and is subject to control by the addition of ferromanganese to the welding rod coating. Obviously some manganese must be volatilized at the high temperatures of the arc and it is a fortunate circumstance that this manganese control is exercised under suitable reducing conditions. It will be noted that the sulphur to manganese ratio is about the same as that found in commercial steel. One of the features of the chemical composition is the silicon content, which is well above that commonly occurring in the welding rod or plate stock. In fact it is about correct for properly made cast steel. It will later be shown that this silicon is largely metallic so that it must have come from the silica content of the covering by the reducing action prevailing in the arc space.

The nitrogen content is satisfactorily low. The author has never found that this small amount is harmful, though it is known that large amounts of nitrogen will make steel brittle. On the other

hand it appears feasible to assume that a small and controlled amount of nitrogen acts as an alloying element to increase the strength without sacrificing too much ductility. The total oxygen content is somewhat above that found in properly made commercial steel, especially those grades with appreciable amounts of manganese and silicon. If one knew only the total oxygen content he would be puzzled by the high quality of this weld metal and would encounter discrepancies on correlating this amount of oxygen with the metallurgical behavior of the metal. By means of the fractional oxygen determinations and microscopic examinations we have found that this oxygen occurs as a fine silica dispersion, and will be discussed later.

Typical mechanical properties of weld metal deposited with the cellulose-covered welding rod and after being reheated to 1200 degrees Fahr. are given in the following tabulation:

Yield Point	40,000 to 45,000 pounds per square inch
Tensile Strength	55,000 to 60,000 pounds per square inch
Elongation, 2 inches	30 to 40 per cent
Reduction of area	45 to 55 per cent
Charpy value	30 to 40 foot-pounds
Endurance limit	30,000 pounds per square inch
Brinell Hardness No.	120

A more complete discussion of the mechanical properties of this type of weld metal and of welded structures which have been fabricated with the cellulose-covered welding rod has been given by Jasper, Andrus and Larson, and hence the engineering phases need not be dealt with here.[7]

Summing up, the properties cited in the foregoing tabulation speak adequately for the excellent quality of this material. It is clear that this type of weld metal is quite sufficient for the purpose of joining two plates of good commercial steel without sacrifice of strength or ductility at the joint. While the tests of the above tabulation represent all weld metal, this characterization is not altered when tests are made across the weld or of the complete structure.

Coming to the microstructure of welds made with cellulose-covered welding rods we enter a field of investigation that has shed much light on the reasons for the superior qualities of this metal, though the field is too broad for complete consideration here.

The macrographs in Fig. 9 show the polished and in Fig. 10 the etched cross sections of such a weld in 1-inch plate stock. These

[7] T. M. Jasper, O. E. Andrus and L. J. Larson, *The Refiner*, April and May, 1933.

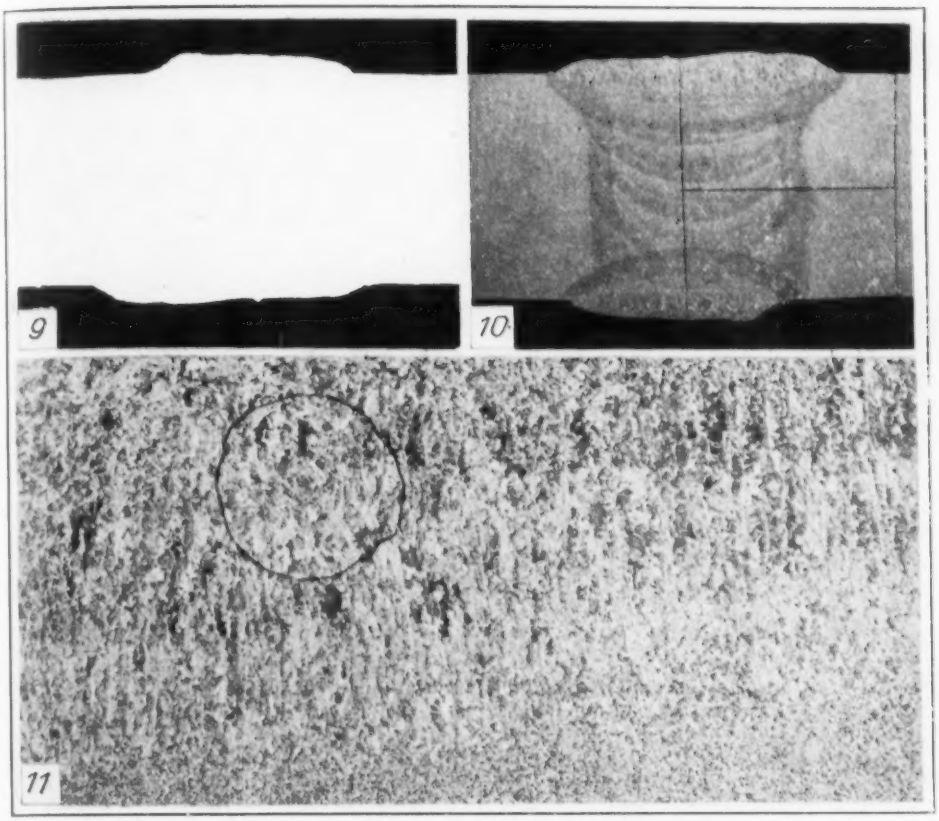

Fig. 9—Cross Section of Weld Made with Cellulose-Covered Welding Rod, As-Polished. × 1.

Fig. 10—Same as Fig. 9, Etched. × 1.

Fig. 11—Same as Fig. 10, Etched. × 9.

may be compared directly with the photographs of bare wire welds. The differences between these two welds favor the former as being of better quality. If these sections be deep-etched in hot acid a striking difference is seen because the bare wire weld is badly attacked and reveals a definitely inferior quality of metal. The macrograph at 9 diameters in Fig. 11 also shows a dense, sound structure.

One of the most interesting features of this weld metal is the type of inclusion. The typical inclusion is so fine that higher magnification is necessary. Fig. 12 shows some of the coarser particles of the fine silica dispersion which occurs throughout the weld. Superficially this dispersion resembles that in the bare wire weld metal, except that there is less foreign material present, and we have found that the usual examination with ordinary white light does not adequately differentiate these types of inclusions. On the other hand polarized light brings out a striking difference as is shown by Fig.

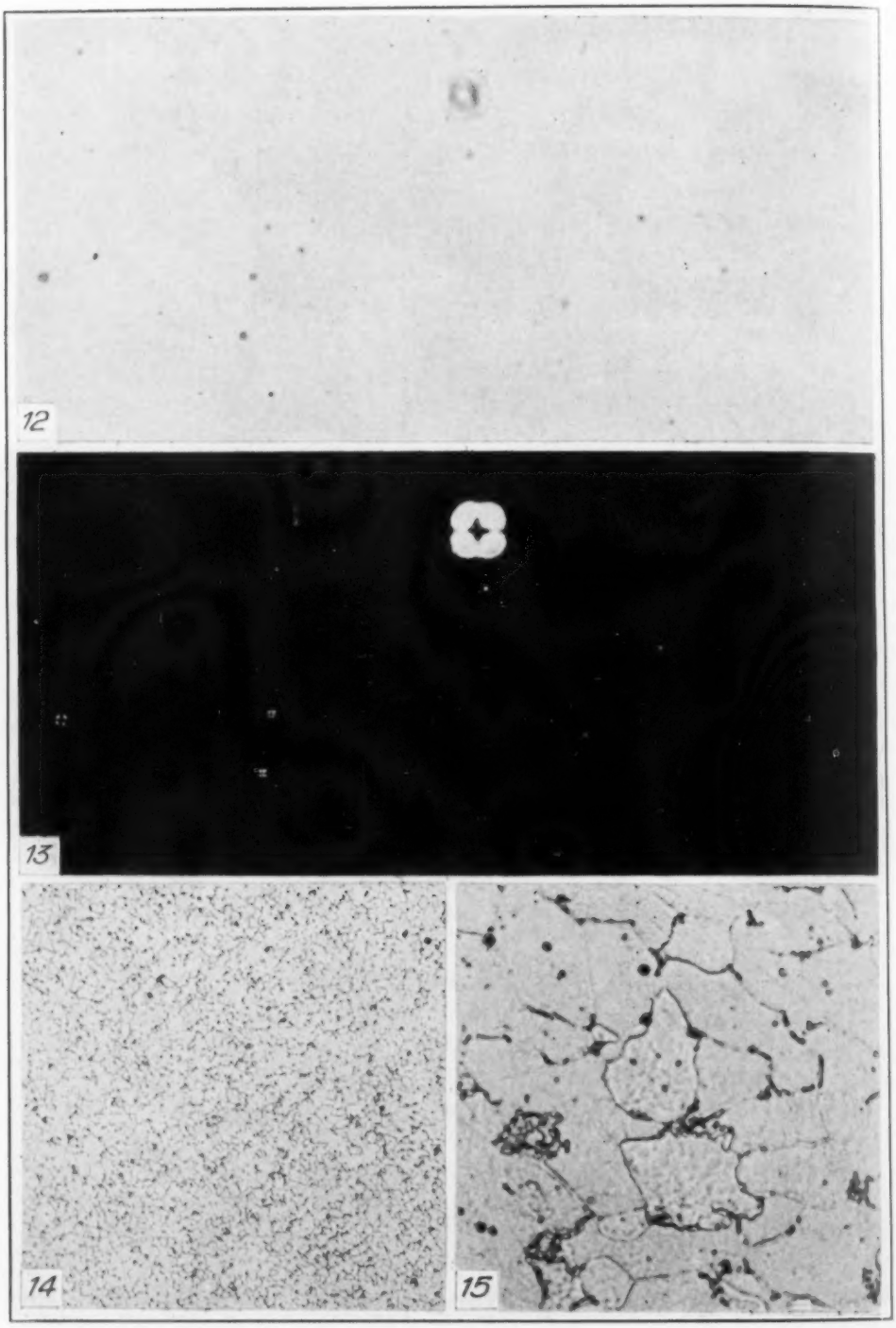

Fig. 12—Silica Dispersion in Weld Deposited with a Cellulose-Covered Welding Rod. × 430.
Fig. 13—Same Field as Fig. 12, with Polarized Light, Crossed Nicols. × 430.
Fig. 14—Weld Metal Deposited with Cellulose-Covered Welding Rod, Etched. × 100.
Fig. 15—Same as Fig. 14. × 1000.

13 which is the same field as that of Fig. 12 when viewed under crossed Nicols.[8] Each one of the inclusions lights up and appears as an optical cross. This examination shows that the inclusions are of a clear glass type and essentially colorless. The inclusions in bare wire weld metal all remain dark under crossed Nicols which shows that they are opaque. Subsequent identification by chemical tests

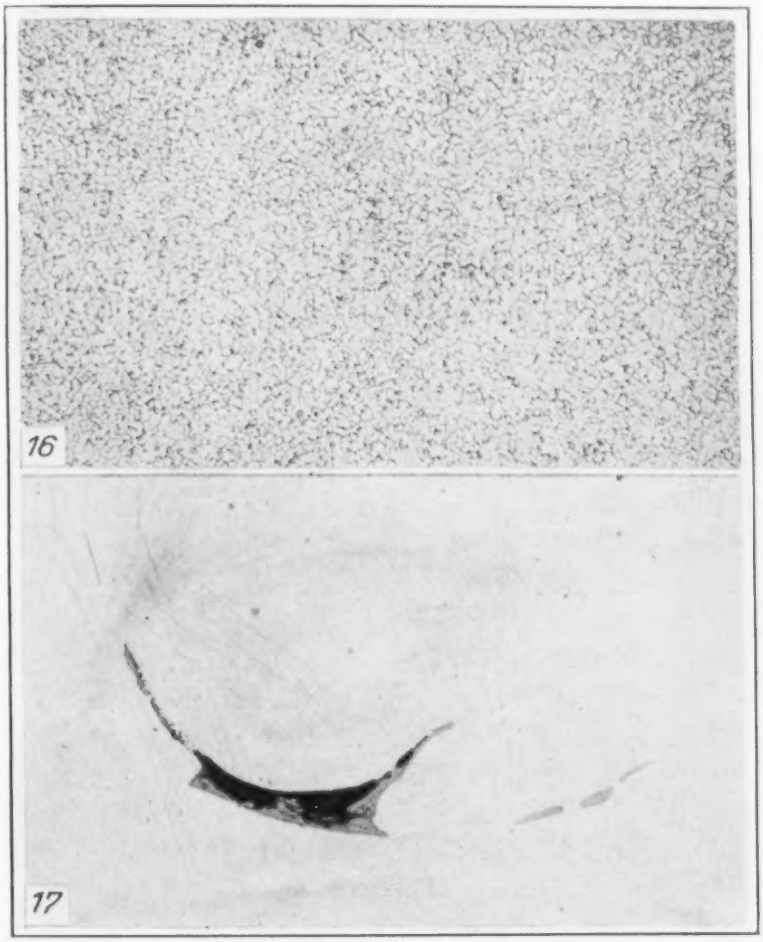

Fig. 16—Junction of Plate Stock and Weld in Weld Made with Cellulose-Covered Welding Rod. × 100. The Left Half is Plate Stock, the Right Half Weld Metal.
Fig. 17—Slag Stringer in Weld Metal. × 100.

reveals them as FeO. Many times the chemical analysis and an examination with polarized light gives sufficient identification of the foreign inclusions.

[8]The use of polarized light is being dealt with separately, in collaboration with M. A. Scheil, and reference is made to that discussion for details. See American Institute of Mining and Metallurgical Engineers, Fall Meeting, 1934.

The typical microstructure of weld metal as deposited by the cellulose-covered welding rod is shown in Figs. 14 and 15. The photomicrographs present a clean cut appearance and show that the structure is very fine. In contrast to the bare wire weld, the junction between weld and plate stock is not marked by a carbide segregation or by a nitrogen pick up. Fig. 16 shows the typical uniform structural gradation at the junction. It is frequently necessary to follow the elongated inclusions in the plate stock and the globular inclusions in the weld to trace the actual junction.

Occurrence of Oxygen in Weld Metal

The determination of the amounts of the various oxides which occur in weld metal has played an important, even unique, role in our studies of weld metal quality and will be discussed separately before proceeding to the complementary microscopic examination of foreign inclusions.

A serious study of weld metal quality made it desirable to analyze for oxygen. Equipment of the latest design was installed and our metallurgical findings were soon being correlated with the "total oxygen" content of the weld samples. This phase of the work was distinctly disappointing. No rational correlation could be found. It was clear that the total oxygen determination was lacking in selectivity. Out of the necessity for securing oxygen determinations which could be satisfactorily used in our metallurgical studies, Dr. Reeve developed a reliable method for determining the "fractional oxygen" contents of the samples.[9] These analyses characterized the weld samples at once as "oxidized," "killed," etc., and agreed perfectly with the results secured by microscopic examination. Thus we were able to account for the metallurgical behavior of the materials. Since then many such determinations have given us a much better understanding of the condition of weld metal (and steel) than we had previously. Fractional oxygen determinations of three different types of weld metal are given in Table I.

The error involved in the fractional oxygen determinations is largely subject to the control of the analyst. This we have considered and feel that the errors involved in our present procedure are small enough to avoid drawing erroneous metallurgical conclusions.

The bare wire weld metal is rather easily characterized as

[9] L. Reeve. Loc. Cit.

Table I
Fractional Oxygen Determinations of Weld Metal

Weld Rod	Bare Wire Per Cent	Slag Coated Per Cent	Cellulose-Covered Per Cent
Oxygen as FeO	0.282	0.208	....
Oxygen as MnO	.....	very small	0.01
Oxygen as SiO_2	0.0004	0.032	0.052
Oxygen as Al_2O_3	0.016	0.017	0.008
Total oxygen	0.298	0.257	0.070

oxidized metal from the large amount of iron oxide and the small amounts of counteracting constituents. It is similar to a heat of low carbon steel which we deliberately oxidized on melting, and which showed the same type of composition and behavior. The weld metal made with the cellulose-covered welding rod is likewise easy to characterize because it contains no iron oxide and, as will be shown later, does contain generous amounts of metallic silicon and manganese. It is thoroughly deoxidized metal. The weld metal from the slag-covered welding rods is not so easily characterized. One might assume from its large amount of iron oxide that it is oxidized metal in the same sense as the bare wire weld metal but, it has been our experience that this type of metal occupies a more or less intermediate position. It will be noted that it contains an appreciable amount of silica and alumina and it seems likely that they tend to counteract the bad effects of iron oxide. The microscope comes to the aid of the fractional oxygen determination and shows duplex inclusions with iron silicate and this metal is closer to wrought iron than to oxidized low carbon steel in its characteristics.

Foreign Inclusions in Weld Metal

Nearly all samples of steel and weld metal contain foreign matter or inclusions of some kind. These are mostly oxides, sulphides and silicates. The study of these foreign inclusions in weld metal has given a valuable insight into its quality and characteristics and some comments will be offered on the point of view which has been the guide. Briefly it may be said that they are first studied as so much "dirt" and then, in conjunction with chemical data, as clues from which may be deduced the proper characterization of the metal. As "dirt," the mechanical effect of inclusions depends on their size, shape, amount and mode of occurrence. We may thus distinguish

broadly three classes of foreign inclusions, (1) large inclusions, generally elongated, (2) small inclusions, variously shaped, and (3) finely dispersed inclusions.

An illustration of the effect of large, elongated inclusions may be made by bending wrought iron so that the bend is parallel to the direction of the slag stringers and noting that it lacks ductility and toughness. This may even show up on forging at an elevated temperature. In this direction the metal is of low quality on account of the large amount, size and unfavorable distribution of the foreign inclusions present. If this same wrought iron be bent so that the bend is at right angles to the slag stringers, it is found to be ductile and tough. Here the metal quality is satisfactory in spite of the foreign inclusions. "Sand streaks" which accidentally become entrapped in ingots for large forgings offer another example of foreign inclusions which affect the metal behavior but in general steel seldom contains such large inclusions or so many of them that its quality is seriously impaired by that one fact alone. A quantitative expression of the bad effects of the larger inclusions, and particularly those of the stringer type, is given in Epstein's method of rating inclusions according to length[10] and about the same thought is contained in Herty's classification of inclusions according to size.[11] In both instances much greater weight is given to the larger inclusions.

In the case of weld metal deposited by bare wire and slag-covered welding rods we have observed that oxide and slag become entrapped in the welds. This is enhanced by the mechanism by which the metal is transferred across the arc and the relatively low temperature which causes rapid solidification. An example of such an occurrence is given in Fig. 17 and it seems entirely logical to ascribe this defect to the welding rod.

The second type of foreign inclusions may be readily disposed of as being innocuous in ordinary steel or weld metal. Such inclusions would receive the lower ratings by Epstein or Herty. Lightner and Herty found that even "extremely dirty steels" by the Epstein rating failed to show a lowering of the impact strength unless the inclusions were large and located directly behind the notch of

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[10]S. Epstein, *Metals and Alloys*, 1931, Vol. 2, p. 186.

[11]C. H. Herty, Jr., TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1931, p. 1.

the test bar.[12] This leads to the thought that the mechanical effects of the inclusions in weld metal may be disregarded, except for the large or elongated type which has just been discussed.

An interesting and important type of inclusion is the dispersion of small globules which occur scattered throughout the metal. The size of the particles is important and in tungsten filament manufacture a special method is followed which insures securing a fine size and uniform distribution. In addition the amount present plays an important role in filament performance and is usually controlled at 1 per cent of thoria by weight. This effect in tungsten has been described by Dr. Jeffries years ago, but the present author wishes to point out that a fine dispersion in weld metal provides an effective barrier to grain growth when the metal is heated to temperatures just below the melting point. Bare wire weld metal contains about 0.9 per cent FeO by weight, or 1.1 per cent by volume, and weld metal deposited with the cellulose welding rod contains about 0.11 per cent SiO_2 by weight, or 0.35 per cent by volume.

Mention of the dispersions raises an interesting point of the mechanism of their formation. The iron oxide inclusions of this type are generally associated with the solubility of iron oxide in molten iron and one is inclined to assume the same origin for the silicate inclusions. The weld metal is highly heated when in intimate contact with silicious material and the possibility exists of dissolving some of the silica. Another suggestion is that oxygen can diffuse into liquid or solid iron and precipitate as globular silicate inclusions. In our laboratory we have studied diffusion phenomena in solid iron and believe we have observed both the diffusion of oxygen with subsequent precipitation on the interior as oxides, and the diffusion of silica under conditions which apparently excluded the possibility of the first phenomenon, though carefully controlled experiments would have to be performed before the various points could be competently verified. In the case of the cellulose-covered welding rods in which the metal is deposited under strongly reducing conditions, as shown by the increase in the silicon content of the deposited metal as compared to the weld rod or plate stock, it seems unlikely that diffusion of oxygen accounts for the silica dispersion. Of course, if silica can dissolve in solid iron, it should dissolve more

[12] M. W. Lightner and C. H. Herty, Jr., "The Transverse Impact Strength of Plain Carbon, Normalized Steels." Cooperative Bulletin 59, Metallurgical Advisory Board to the Carnegie Institute of Technology.

readily in molten iron, and we could account for the silica dispersion on that basis.

Important as the mechanical effects of foreign inclusions in weld metal may be, the clues which their identification offer as to the condition of the metal are equally significant. Thus bare wire weld metal is charged with oxygen as iron oxide; in other words it is "oxidized" metal and is similar to Bessemer metal after blowing but before being deoxidized. We may confidently expect it to show the metallurgical characteristics of oxidized metal. The foreign inclusions in weld metal from the cellulose-covered rod are practically colorless silica or silicates. If iron oxide were present in small amounts the silicate inclusions would be colored, and if it were present in large amounts as free FeO, we would recognize it as a constituent of the metal. This metal is thoroughly "deoxidized" and the inclusions give the strongest evidence of that fact. We may likewise expect this metal to show the characteristics of well deoxidized metal.

Upon closing this discussion of foreign inclusions in weld metal, we offer some of our experience with methods of determining them quantitatively, along with some conclusions which have been drawn on the basis of these results.

The inclusion-count method suggested itself as a means of determining the amount of foreign matter present, as the shape of the particles lent itself to this type of determination. While we secured reasonably good data, the inclusion-count method did not seem to offer as much promise as the method of electrolytic extraction which had recently been developed at Pittsburgh and was dropped in favor of the latter. Electrolytic extraction works very nicely on weld metal deposited by the cellulose welding rod which contains mainly silica and alumina as foreign inclusions. The amounts of manganese, silicon, and aluminum recovered in the residues as their oxides, expressed as percentages of the weight of sample dissolved, were as follows: Manganese, 0.01 per cent; Silicon, 0.05 per cent; and Aluminum, 0.006 per cent.[13] We presume that some of this manganese may occur as the sulphide. By means of these amounts of silicon and aluminum which occur as oxides, and the total amounts of these elements in the weld metal as shown by chemical analysis,

[13]It may be of interest to note that Mr. Roach developed a reliable spectroscopic method for determining aluminum. It is probably our most accurate method for determining segregations of this element in steel.

we can arrive at an estimate of the condition of the metal. These calculations show that about 80 to 85 per cent of these elements occur in the metallic state in the weld metal, which is very good evidence to corroborate the previously stated conclusion that this metal is well killed.

Inasmuch as silicon occurs in weld metal deposited with bare wire and slag-covered welding rods, its degree of oxidation can likewise be used to study the condition of those metals. Calculations similar to those above showed that 98 per cent of the silicon is oxidized in a weld of the latter type and 100 per cent in a weld of the former type. This difference cannot be significant and it is clear that in both metals the silicon occurs oxidized as silica. Similar determinations made on commercial low carbon steel show that the condition of its silicon is more nearly the same as that of the weld metal deposited with the cellulose-covered rod. Of course the reactions responsible for the condition are different in the two cases.

To return now to the point of view used in our study of weld metal and of foreign inclusions, the microscopic methods show the manner in which they occur, their size, shape, distribution and type, and the fractional oxygen determinations give the quantitative amounts of the various oxides of which they are composed. One feature is missing in the quantitative determinations and that is the amounts of iron oxide and manganese oxide combined with silica to form silicates, but here the polarizing microscope and one's experience in the field assist in drawing proper conclusions.

Metallurgical Characteristics of Weld Metal

Studies of the composition and structure of weld metal bring out marked differences between different types of weld metal. It has also been interesting to note the way in which these characteristics correlate with the metallurgical behavior of the metal, as will now be shown.

The McQuaid-Ehn Test—Investigators have shown by their published accounts that bare wire weld metal is definitely abnormal in grain-size and in structure. It has also been intimated that some modern welds are normal in this respect.[14] This is undoubtedly sufficiently well known to obviate any necessity here to consider the mat-

[14]See, for example, W. Zieler, *Stahl und Eisen*, Vol. 52, 1932, p. 236, and F. R. Hensel and E. I. Larsen, *Metals and Alloys*, Vol. 3, 1932, p. 250.

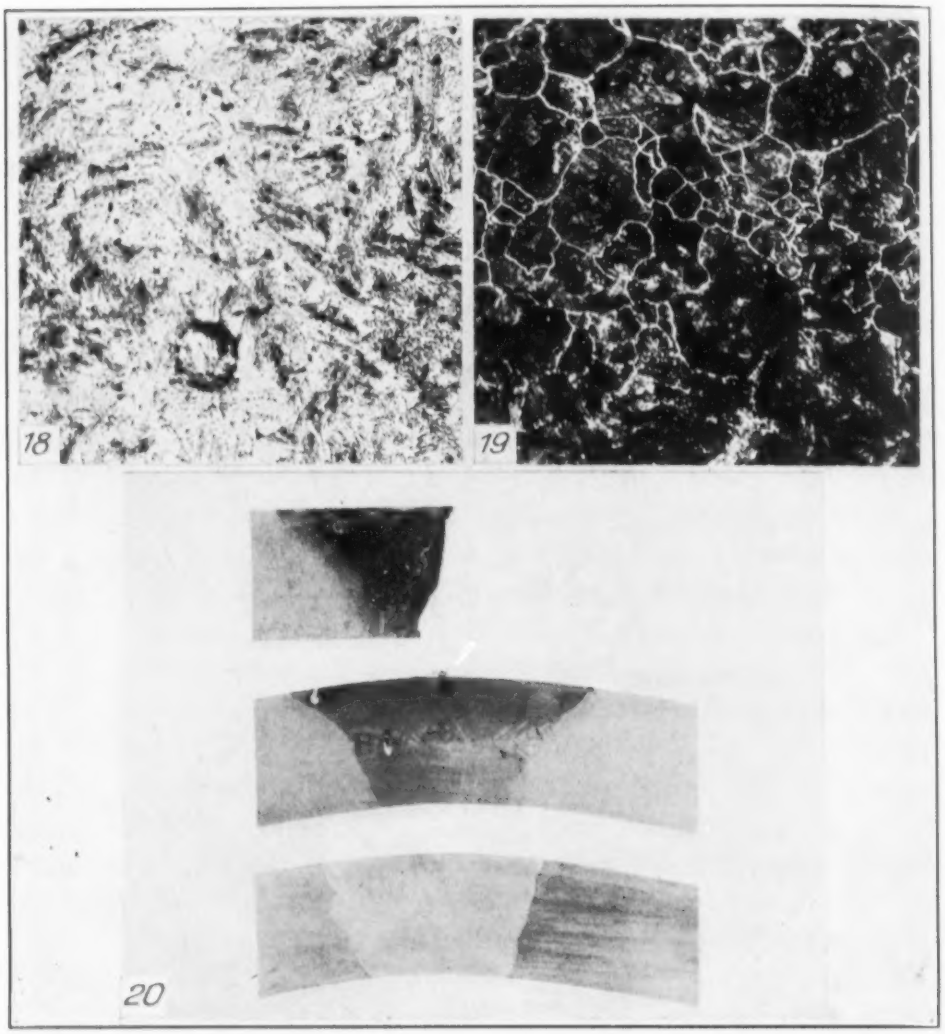


Fig. 18—McQuaid-Ehn Carburizing Test of Bare Wire Weld Metal, Case Structure. × 100.

Fig. 19—Same as Fig. 18 for Weld Metal Deposited with the Cellulose-Covered Welding Rod.

Fig. 20—Fry Test with Weld Metal Samples:
Top—Bare Wire Weld.
Center—Weld Metal from Flux-Coated Welding Rod.
Bottom—Weld Metal from Cellulose-Covered Welding Rod.

ter in detail. Fig. 18 represents bare wire weld metal after being carburized according to the standard McQuaid-Ehn test for 8 hours at 1750 degrees Fahr. and allowed to cool in the furnace. The result obtained by a similar treatment on weld metal deposited with the cellulose-covered weld rod is given in Fig. 19. Thus it is seen that the latter type of weld metal is returned "normal" by this test. Various other types of metal were likewise tested for normality.

When only the total oxygen contents of the metals were available the picture was decidedly confused and we even made an attempt to correlate the normality with the nitrogen content. This, too, was unsatisfactory and we returned to the idea that oxygen must be responsible for the abnormal structures. This experience was one reason for the strong desire to secure fractional oxygen determinations. By means of the subsequent study, which extended over a wide variety of metals, we were able to correlate this behavior with the amount of iron oxide in the metal. A series of metals or irons in which the oxygen, as iron oxide, varied from nil to about 0.2 per cent showed a uniform change in structure between the limits shown in the photographs reproduced here. The limiting case was a melt of pure iron which we melted with an addition of iron oxide and which showed the same abnormality as bare wire weld metal.

Hot Shortness Tests—The degree to which weld metal is subject to hot shortness is an important characteristic of the metal, particularly with multipass welds in thick plates. Obviously the weld metal must cool down from the solidification temperature while subject to a constraint by its union with the plate stock. Ever since steel ingots have been cast and rolled and castings have been made in steel, this property has been a vital feature of steel metallurgy. Weld metal is no exception, and we may list hot shortness as one of the factors which controls the use which may be made of welding.

Reference has been made to cracks which are observed in bare wire weld metal but this evidence of hot shortness has been supplemented by systematic tests on various weld samples and on special samples of iron and steel. Either the top or the bottom half of a slice such as is illustrated in the photomacrographs was used as a test sample. After being heated to the test temperature (1050 degrees Cent.) it was put through three successive tests, between which the sample was reheated to the test temperature. First the bar was bent 90 degrees and secondly 180 degrees, whereupon it was broken in two when cold. Finally one-half was flattened by one blow of a hammer into pancake form. The bare wire weld metal fractured on the first bend and frayed badly on the edge of the pancake. Weld metal deposited with the cellulose-covered rod passed all tests with no sign of hot shortness, even though the final test was severe. This metal was also tested at other temperatures to cover the range over which oxygen is supposed to be effective. Good commercial steel also passed the tests satisfactorily, while the special heat of pure iron

which had been oxidized during melting (high iron oxide) was found to be hot short.

Having shown these differences between the different types of metal, it is of interest to assign a cause to the behavior. A perusal of the literature would suggest iron oxide as a most likely cause, particularly the story of Mushet's contribution to the success of the Bessemer process which consisted of adding manganese to the blown metal.

Our tests were performed on samples whose chemical analyses were well known and whose fractional oxygen content and foreign inclusions had been determined. It was found that those samples were hot short whose predominant constituent, besides iron, was iron oxide. Other samples which also had a generous amount of iron oxide but which also had some silica showed some hot shortness but not at all in proportion to their content of iron oxide. Samples which had no iron oxide, but which also had metallic manganese and silicon, were not hot short.

The literature also mentions the effect of sulphur in producing hot shortness, but its effect comes at an appreciably higher temperature than that produced by iron oxide; i.e., about 1325 degrees Cent. In some early work of the present author on the effects of various additions to steel, this effect was found. It is also pointed out that the combination of iron oxide and sulphur is harmful. Niedenthal, in a systematic study of the effects of iron oxide and sulphur both separately and in combination, shows that the sulphur effect is superimposed on that due to oxygen.[15] The work of Niedenthal is quite clear in bringing out the effect of oxygen over the range of 900 to 1100 degrees Cent. At one time during these tests we had occasion to study the effect of iron oxide and sulphur in combination in weld metal. In the series of hot shortness tests it was found that the weld metal was hot short over a wider temperature range than bare wire weld metal and was also of inferior quality. It was obvious from this test that the combination of iron oxide and iron sulphide in the weld metal is definitely harmful and even more so than iron oxide of bare wire weld metal. In general the tests confirmed earlier work on the effects of these two constituents.

Deep Etch Test and Sulphur Printing—The results of deep etch tests have already been referred to as differentiating clearly

[15]A. Niedenthal, *Arch. Eisenhuettw.*, Vol. 3, 1929, p. 79.

between bare wire weld metal and that deposited by the cellulose-covered welding rod. Sulphur prints show no difference and the circumstance that both types of weld metal are low in sulphur is not the only reason for that. Actually the Baumann print, though it is ordinarily an excellent means of revealing macroscopic segregations, does not react to the weld metal even though the time of contact be greatly increased. The cadmium-copper print gives the same negative results. This behavior seems to be associated with the fine dispersion in which the sulphide occurs. The only weld we have examined that gave a positive reaction to the sulphur print was that which contained the combination of iron oxide and iron sulphide. Its reaction was vigorous.

Fry, or Strain Aging Test—The Fry test is carried out by moderately bending or deforming the test bar at room temperature, heating to 250 degrees Cent. for thirty minutes, and etching a section through the strained portion by Fry's macroscopic reagent. The results secured with three different types of weld metal are shown in Fig. 20. The bare wire weld metal was so brittle that it would not stand the initial bending and it etched dark all over. The weld metal made with the cellulose-covered rod showed no Fry lines and hence is classed as non-aging by this test. Weld metal deposited by slag-covered welding rods shows well defined Fry lines along the neutral axis.

Age Hardening Tests, Quench Aging—Additional slices were taken from the weld samples for this test. These were quenched in water from 600 degrees Cent. after one hour and their hardness tested directly after quenching and after aging three days at room temperature. This temperature was lower than we had previously used in similar studies on low carbon steel but it was the same as that used by Hensel and Larsen in a similar study of weld metal[16] and it was thought there would be some advantage in having a direct comparison with their results. Some low carbon steels show an increase in hardness after aging at room temperature while others do not. In other work of this kind we have observed this effect over the range of carbon from 0.02 to 0.10 per cent. A positive reaction to this test does not mean that the metal is necessarily of correspondingly low quality but it does show that that metal contains constituents which dissolve on heating and precipitate on standing at room tem-

[16]F. R. Hensel and E. I. Larsen, TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 639.

perature, to subscribe for the moment to the hypothesis designated by the term "precipitation hardening." Table II gives the results obtained with welds made with the bare wire and cellulose-covered rods.

Table II
Age Hardening of Weld Metal

	Rockwell Hardness							
	Top Pass		Body		Aff. Stock		Plate Stock	
	1	2	1	2	1	2	1	2
Bare Wire	99	102	103	105	90	96	75	78
Cellulose-covered	77	77	78	80	81	83	79	82

Note: The Rockwell tests used the $\frac{1}{8}$-inch ball and 100-kilogram load. The reading (1) was made directly after the quench and (2) was made three days afterwards.

It is believed that both types show an aging effect though the bare wire weld has a high initial hardness. The effect at the affected stock of the bare wire weld is probably largely due to absorbed nitrogen, and that in the weld made with the cellulose-covered rod to carbon. Similar tests made with weld metal deposited with the slag-type of weld rod showed a more marked aging effect in both top pass and body of the weld.

Summary

It is realized that much more could be written about these different types of weld metal and about the features of the processes which are responsible for their characteristics, but this account should be sufficiently complete to serve as an introduction to the actual quality of the different metals. The bare wire weld is strong when properly made and this seems to be its chief virtue. It definitely lacks most of those properties and qualities which characterize the common commercial steel which it is used to unite. This has long been recognized and must control and limit the uses which may properly be made of this type of weld. Metal deposited with the cellulose-covered welding rod is seen to possess strength, ductility and toughness to a degree which is entirely adequate for any service for which it is properly designed. It is thus capable of being used even where the requirements of metal quality are stringent and without the limitations that must be placed on bare wire weld metal.

In closing, it is a pleasure to acknowledge the assistance of M. A. Scheil, H. Langebeck, H. Jaeger, and others of the Research and Engineering Department who have co-operated in this study, and to express appreciation to the A. O. Smith Corp., for permission to publish these results.

DISCUSSION

Written Discussion: By Hugo W. Hiemke, Bureau of Engineering, Navy Department, Washington, D. C.

The contribution which Dr. Hoyt has made to the science of arc-weld metallurgy marks an epoch in the development of this relatively new branch of metal science. The value of the work is enhanced by the knowledge that these data are the crystallization of thought coming from 15 years of experimental work at the laboratories of one of the pioneers in the field.

Since 1925, the success of the A. O. Smith Corporation in producing ductile arc-weld metal has stimulated research in other laboratories to such a degree that many other processes have been developed. All these processes are basically similar because they use heavily coated electrodes for the purpose of excluding the atmosphere from the arc space during welding. However, the coatings themselves may be divided into two major groups: (1) organic coatings, which incorporate an appreciable quantity of carbohydrate material, such as cellulose, in a mixture of inorganic materials; and (2) inorganic coatings, which depend on a properly proportioned slag mixture to protect the weld.

Dr. Hoyt has very ably presented the essential characteristics of bare wire weld metal and weld metal deposited with the cellulose type of covered electrode. However, the description introduced of weld metal deposited with a slag type of weld rod, in the opinion of the writer, does not do justice to the possibilities of the modern inorganic type of electrode.

The Naval Engineering Experiment Station,[1] at Annapolis, Md., has had the opportunity of testing a great number of welds made by various processes in connection with the requirements for approval of a welding process prior to the fabrication of naval machinery. The tests ordinarily made include tension of all-weld metal, tension across the weld, bend tests, Charpy impact test, chemical analysis, and studies of the inclusions and the microstructure. Additional tests which have been made in special cases include fatigue tests, creep tests and tension impact tests. While these tests are not as exhaustive as the ones made by Dr. Hoyt, they, nevertheless, represent in a large measure the tests ordinarily made by metallurgists to judge metal quality. The attached Table I is introduced as a set of typical properties of welds made with a recently developed inorganic coating.

The low nitrogen content of the metal is indicative of quite adequate exclusion of atmospheric influence in the arc. The high silicon and manganese give a clue, at least, to the successful exclusion of iron oxide from the weld. It seems reasonable to suppose that the oxygen which is present in this weld will be combined largely as silica and manganese oxide. It will be noted, however, that no oxygen analysis has been reported. The writer considers the fractional oxygen analysis developed by Dr. Reeve and Dr. Hoyt as an exceptionally valuable tool for demonstrating fundamental differences between metals. It is regretted, therefore, that this analysis cannot be included in this discussion.

Referring to the physical properties (Table I), it will be noted that the weld metal combines high ductility and toughness with high tensile strength.

[1]The data and photographs reported in this discussion were prepared by W. C. Stewart, metallurgist of the Naval Engineering Experiment Station.

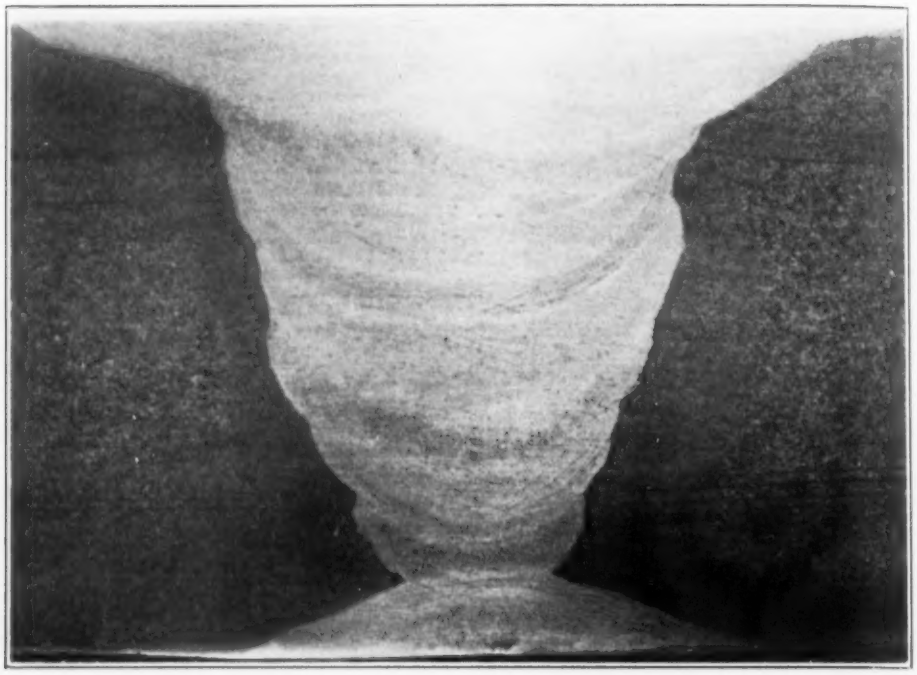


Fig. 1—Photomacrograph of Weld Illustrating Its General Uniformity and Soundness of Deposited Weld Metal. × 2.5.

Such excellent properties, in themselves, characterize the weld as quality metal.

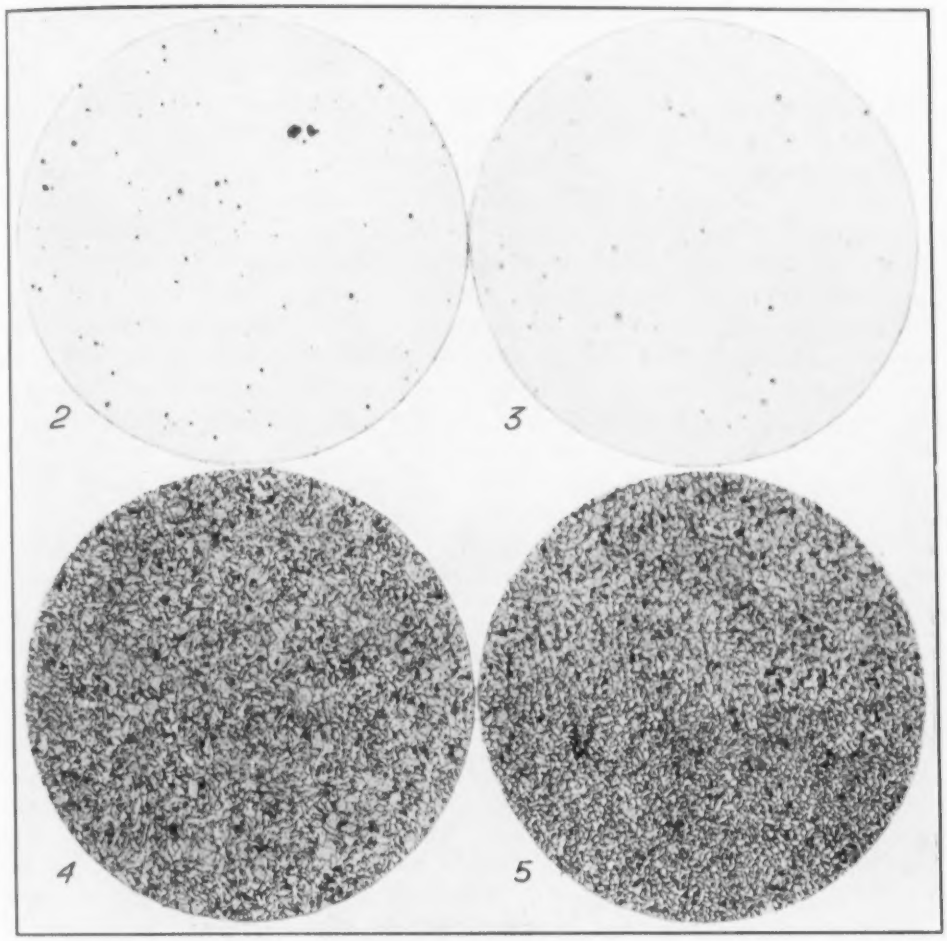
Illustrations of the weld are reproduced as Figs. 1 to 5 of this discussion. Fig. 1 shows a macrograph of the weld illustrating its general uniformity and soundness. Figs. 2 and 3 are photographs of the unetched weld at 100 and 400 diameters, respectively. It will be noted that the inclusions are present in large numbers, but the typical inclusions are small rounded and uniformly disposed.

Table 1

Chemical Analysis Per Cent		Physical Properties
Carbon	0.07-0.12	Yield point 50,000-60,000 p.s.i
Manganese	0.40-0.70	Ultimate strength 65,000-80,000 p.s.i
Silicon	0.15-0.25	Per cent Elongation in 2 inches—20-35 per cent
Phosphorus	Less than 0.025	Per cent Red. in Area—40-60 per cent
Sulphur	Less than 0.040	Charpy value—ft.-lb.—20-40
Nitrogen	Less than 0.035	Brinell hardness 140-175

In view of the excellent physical properties of this material, it must be assumed that such a distribution of inclusions is not harmful. Fig. 4 shows the etched weld at 100 diameters. The grain is quite fine, and there are no nitride needles. Reference to Fig. 1 shows that this is the typical structure, each bead being refined by its successor. Fig. 5 shows the structure at the fusion zone.

Weld metal of the quality indicated by these tests is admirably suited for joining boiler plate, without impairing the safety of the completed structure. Indeed, it has been successfully used in such service for the past five years.



Figs. 2 and 3—Photomicrograph of Unetched Weld Metal at 100 and 400 Diameters Respectively.
Fig. 4—Photomicrograph of Etched Weld. × 100.
Fig. 5—Photomicrograph of Weld Metal at Fusion Zone. Etched. × 100.

Written Discussion: By S. V. Williams, Struthers-Wells Co., Warren, Pa.

This paper is indeed timely, as inherently it is the metallurgist's work to reduce modern welding from an art to a science. The American Society for Metals is to be congratulated on sponsoring papers of such scientific value on the metallurgy of arc-deposited weld metal.

That we should not all see the same definition is well for the establishing of scientific facts. From my vista, the modern weld rod is the most flexible tool man has by which metals can be joined together by purely metallurgical means. If the design of our weld rod does not create these metallurgical means, our weld will be found wanting in its mechanical properties, even though the parent metals be of the highest quality.

This rightly infers that the quality of our metals being joined affects the quality of the arc-deposited weld metal. This I am sure the author realizes. Furthermore, I am sure he realizes that the metallurgy of arc-deposited weld

metal in heavy thicknesses of metals requires a more exacting tool than lesser thicknesses. In other words, our metallurgical effects must be balanced in the melting, solidification, and subsequent heat treatment periods of welding. The design of our weld rod largely controls this balancing.

The bare wire weld rod failed in the control of all three periods of welding. This paper very aptly brings out the reasons why it failed. The design of our modern weld rod must correct these deficiencies of the bare wire rod.

We concur with the author that the elongation and ductility of a bare wire weld made with plates of 1 inch thickness are lower than that on a 0.25 inch plate. Normally, we should expect with this lowering an increase in ultimate strength, but find it 10 to 20 per cent lower. This indicates the presence of shrink cracks in the weld metal, caused by the hot shortness of the metal, and the failure of subsequent layers to stress-relieve the residual stresses of previous deposited layers. This failure is often evidenced by the cracking of such welds when completed or partially completed.

The chemical analysis of the bare wire arc-deposited metal shows it to be highly oxidized—if not a burnt metal. Even with a high degree of mechanical working, it is difficult—if not impossible—to overcome this by heat treatment. The bare wire rod is incapable of creating the necessary thermal or heat units to accomplish this.

Modern weld rods are so designed as to generate a gaseous shield from the constitutents of its covering. The residual slag-forming constituents gather at the back of the pool formed by the melting and fusing of meeting metals. What the nature of this gaseous shield and residual slag should be depends on the degree of purification and alloying we are desirous of obtaining in our arc-deposited weld metal.

An inert gas would greatly alter the arcing characteristic of the weld rod, and be very unstable. It must be an active gas. The author has pointed out that the arc ionizes the gases. If the gas ionizes, it must again associate, and it is at this stage that it should not have any affinity for our metal. Furthermore, it is desirous that its affinity for oxygen and nitrogen be greater than that of the metal.

The degree of ionization of the gaseous shield has a decided influence upon the resistance of the arc, and therefore its stability and the amount of energy consumed in the arc to be dissipated as heat units. This function of the arc is the crux in the design of our modern weld rod, for unless the necessary heat units are created at the point of our electrode, our metallurgical means of joining metal are destroyed.

A word about the residual slag. It generally plays a secondary part, because of the period of time employed. If sufficient heat is created in the pool referred to above, this slag can have beneficial effects, if metallurgically balanced. Certainly, the heats of formation of its constituent components must be higher than the heats of formation of the oxides of the molten metal, if this metal is to be improved.

In short, in modern welding, are we not making steel at the point of our weld rod? Furthermore, are we not teeming this steel in an entirely new manner? The structure finally developed clearly indicates this, when the chemical analysis of the metal is made.

In passing, it should be pointed out that the metallurgy of the metal of the affected zone is also very important in the overall efficiency of our weld. This is particularly important if the weld is to be subjected to severe corrosion.

Written Discussion: By C. E. Plummer, technical director, chemical and metallurgical engineering department, Robert W. Hunt Co., Chicago.

Dr. Hoyt is to be congratulated upon the fine way he has presented this paper, which has added considerably to the subject of foreign inclusions in iron and steel. In our consulting work, we have had occasion to make microscopic studies and physical tests of weld metal made by the three methods outlined in this paper. Our results verify those given by Dr. Hoyt. The following are some typical results obtained in our laboratory on the physical properties of weld metal made with a shielded arc.

Sample Marked	1	2	3	4
Tensile Strength, lbs. per sq. in.	61,040	59,050	59,710	57,770
Elongation in 2 inches				
Amount	0.57	0.56	0.63	0.61
Per cent	28.5	28.0	31.5	30.5
Specific Gravity	7.81	7.80	7.792	7.81

The "fractional oxygen" method which reports separately the amounts of oxygen which are combined with iron, manganese, silicon and aluminum, respectively, is an important stride forward in the study of foreign inclusions.

Dr. Hoyt's broad experience in metallography and his study of inclusions in iron and steel has resulted in producing a paper which is hard to criticize any way but favorably.

Written Discussion: By John L. Burns, Republic Steel Corporation, South Chicago, Illinois.

Since Dr. Hoyt covered such a vast field in his excellent paper, his remarks on some of the details were necessarily brief. I have particular reference to the age-hardening phenomena.

The temperature of maximum solubility of nitrogen in alpha iron is around 580 degrees Cent. (50 per cent nitrogen) while that for carbon is 720 degrees Cent. (0.035 per cent carbon). The room temperature solubility of nitrogen is usually given as 0.015 per cent, while that for carbon is usually stated as 0.006 per cent. Both the nitrogen and the carbon in the bare wire weld are present in greater quantities than their respective room temperature solubility values. In the weld deposited with the cellulose-covered wire, the carbon is present in a greater quantity than its room temperature solubility, while the nitrogen is lower than its room temperature solubility.

Obviously, in the bare wire weld both nitrogen and carbon may play a part in the age-hardening phenomenon, while in the weld deposited with the cellulose-covered rod only carbon could play the part.

It should be noted too, that in the quenching treatment the samples were not brought to a sufficiently high temperature (in the alpha iron range) to allow all of the possible carbon to go into solution. Furthermore, as Dr. Clough[1] has shown, in ordinary water quenching, a large portion of the nitrogen precipitates during the cooling operation. This fact is brought out by obtaining a decidedly lower hardness reading after quenching in iced brine. The resultant

[1]J. B. Clough, Doctor's Thesis—Harvard University.

room temperature aging is greater in the latter case. This accounts in a large part for the high initial hardness of the bare wire weld metal.

A third factor which should be considered in the comparison of the two rods is the rate of hardening of iron-nitrogen alloys as compared to iron-carbon alloys.

Iron-nitrogen alloys complete their room temperature aging after 48 hours,[2] while iron-carbon alloys require about 30 days. Naturally, a three-day test would be unfair as a comparison of the age-hardening characteristics of the two metals. This is not intended as a criticism of the present paper because no such study was intended.

There is no actual separation of a phase or precipitate during the room temperature aging of iron-carbon or iron-nitrogen alloys as evidenced by X-ray diffraction measurements. In this respect age-hardening in these systems behaves as does duralumin during room temperature aging. However, the electrical conductivity in the former alloys increases during aging in the former cases, while a decrease is recorded during the room temperature aging of duralumin.

Oral Discussion

DR. C. H. HERTY JR.:[3] I would like to point out something that is of great interest to me. In Dr. Hoyt's paper it appears that all he has done is to make an open-hearth heat in a very short space of time at a very high temperature. The metallurgy of the welding process is simply a steel-making process, removed somewhat from ordinary conditions in which we think of making steel, and it makes one wonder from the looks of the tests that he has carried out (and which will be reported a little later) whether one might possibly make certain tests in weld metal before proceeding to large scale tests of open-hearth metal.

C. T. PATTERSON[4]: I agree with Dr. Herty's suggestion in regard to the idea that in arc welding we are making steel in a little open-hearth furnace, and I am somewhat disappointed that Dr. Hoyt did not show us more of the high magnification studies. Looking at the picture of the weld, you see very much finer grain structure than in the plate. If you will just take 1000 or 2000 magnifications and compare that with 250 or 500 in the plate, you discover the remarkable similarity in structures of the weld metal and the plate, giving due allowance for the size. That study I commend to all of you who are interested in the improvement of welds or more knowledge of what you have when you have to use welds. I wish Dr. Hoyt would present some high magnification studies of these welds in some future paper.

T. N. ARMSTRONG[5]: Dr. Hoyt is to be congratulated for identifying inclusions. Most of us who have dealt with inclusions in arc deposits have done it on a quantitative basis rather than a qualitative basis. It appears to me that Dr. Hoyt's defintion of modern arc welding is rather narrow in its limits. While it is true that cellulose-covered rods have certain definite advantages over the mineral-coated rods, there is one advantage that the mineral-coated rod has over

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[2]J. L. Burns, A.I.M.E., Iron and Steel Division, August, 1934.
[3]Bethlehem Steel Co., Bethlehem, Pa.
[4]Semet-Solvay Co., Syracuse, N. Y.
[5]Norfolk Navy Yard, Portsmouth, Va.

the cellulose-coated rod. We find that the quantity of inclusions made with mineral-coated rods usually is less than that made with cellulose- or organic-coated rods, and also there is a type of defect in deposits made from organic rods that is not quite so prevalent in the deposits from mineral-coated rods. This is on account of the characteristics of the two rods. Of course we have a gas that acts as a reducing atmosphere around the deposit made with organic coatings. The salt in the mineral-coated rods acts as a reducer, so if the operator does not conduct the welding exactly as he should, he is apt to get gas inclusions. The gas formed by the coating is likely to be trapped in the deposit and not have a chance to come out. I think you will find this condition is more prevalent with organic coatings than with mineral coatings.

Author's Reply

Aside from thanking those who have so liberally and willingly contributed their own share to the discussion of this subject, there is not very much more for me to cover here. Dr. Herty referred to the similarity between the welding operation and open-hearth melting. If he could have seen the use that we made of all his bulletins on open-hearth furnace practice he would have appreciated that we considered likewise that there was a striking similarity. We have found those publications to be extremely valuable in diagnosing many of the characteristics of weld metal.

Various gentlemen have referred to a certain type of weld metal which was not under discussion in the paper, and all I can do is to thank them for making their contributions. I am sure that what they have said will make a valuable addition to the material in the paper, and it is possibly a little unfortunate that those descriptions were not as detailed or as specific as these which are given for the types of weld metal that we are discussing.

Mr. Armstrong stated that weld metal made with the mineral-coated weld rods was cleaner than weld metal made with the cellulose-covered rods. The paper attempts to bring out that what might be called dirt, but which I prefer to call a "beneficial dispersion," is really a good thing. I believe that while the total oxygen content is made to look a little high, around 0.06 or 0.07 per cent oxygen, when you consider the form in which it occurs, I see no reason for wanting to eliminate it. It is well known in tungsten metallurgy that a dispersion of thoria in the tungsten filament is very beneficial. It is added deliberately and the effects that come from that addition are very positive. The silica dispersion in weld metal is of the same type as the thoria dispersion in tungsten and I believe should be regarded as a beneficial dispersion.

The other gentlemen have raised some important points. Mr. Williams refers to plate stock and the heating effect along the weld band, which naturally has been studied quite a bit, but inasmuch as the paper does not attempt to describe those effects, I do not believe I shall attempt an answer. I really would have to write another paper, those effects are so important.

Mr. Hiemke makes a distinction between two types of heavily coated electrodes, those which use cellulosic or organic constituents and those which use inorganic constituents in suitable proportions. The paper attempted to describe weld metal deposited by the former type of weld rod, and, for comparison, introduced some data on weld metal deposited by the straight inorganic rod of

an earlier type. Mr. Hiemke contributes data on weld metal deposited by the "modern" inorganic type of weld rod to show that metal of excellent quality can be deposited by that type of weld rod. Although the data he quotes are not as complete as might be desired, his contribution is a valuable addition to the subject matter of the paper. Personally, I should like to have nitrogen less than about 0.015 per cent, instead of the 0.035 per cent quoted, for it is known that nitrogen is capable of producing certain aging effects. This phase is covered in the paper and it would be of interest to learn how the material of Mr. Hiemke's tests responds in similar treatments.

Dr. L. Reeve wrote likewise stating that excellent weld metal can be deposited by modern or improved types of inorganic weld rods whose constituents are properly proportioned. Dr. Reeve further points out that the definition I used of "modern" arc welding is open to criticism in that it suggests that to do good welding one must use the cellulose type of weld rod. While it might be of interest to learn the accuracy of my presumption in stating the definition, it would be of greater interest to secure complete descriptions of weld metal which is deposited by other types of "modern" electrodes. Dr. Reeve states, for example, that such electrodes operate with a thick slag, which brings up the point raised in the paper about the entrapment of massive slag stringers in the deposit when welding with rods of the slag type.

Again Mr. Armstrong states that the mineral-coated rods produce weld metal that contains less foreign inclusions than that from cellulose-coated rods. This is at variance with the photomicrographs of Mr. Hiemke which indicate the opposite. Mr. Armstrong and Mr. Hiemke must be discussing different types of inorganic rods. In view of the evidence of the paper the smaller amount of inclusions may not be an advantage, in fact that would be doubtful, but this all should be cleared up by more complete descriptions of weld metal as deposited by the various types of inorganic rods.

The material proper of the paper seems to represent the quality of weld metal as deposited with the bare wire and the cellulosic type of weld rod in a satisfactory manner, as judged by the discussions. I am particularly indebted to Mr. S. V. Williams who has contributed from his wealth of experience in this field to give us a fine analysis of the metallurgy of welding. I was also greatly interested in the comments of Mr. Plummer to the effect that he verifies the findings of the paper and that he uses about the same metallurgical criteria.

Finally, Dr. Burns adds interesting comments which are pertinent to aging phenomena in weld metal. These should be carefully considered in a study of this phase of welding. Some weld metals represent quite complicated systems with carbon, oxygen, nitrogen and those faithful friends, sub-microscopic impurities, ready and available to produce aging effects following both heat treatment and mechanical strain.

NONMETALLIC INCLUSIONS IN STEEL

Part I. Products of Deoxidation

By Stephen F. Urban and John Chipman

Abstract

Part I contains a description of the nonmetallic inclusions in steels prepared by the addition of deoxidizing elements to liquid iron saturated with oxygen. The effects of heat treatment and of forging upon the structure of the inclusions is described.

The ore microscope has been used to study inclusions in a polished specimen by the aid of polarized light. A new technique has been developed by means of which individual small inclusions are removed from the steel and their refractive indices measured. Both of these methods have proved useful in the identification of certain types of inclusions.

Subsequent parts will deal with sulphide, oxide-sulphide, and nitride inclusions and with etching methods for their identification.

IN tracing the origin of nonmetallic inclusions in steel and in studying methods for their control in steel-making practice, it is often a matter of importance to be able to determine the nature of the individual inclusions. This task is rendered difficult by the small size of the majority of these bodies and the consequent inapplicability of the customary quantitative methods. An approach toward a solution of this problem may be obtained through the microscopic study of inclusions in steels prepared under such carefully controlled conditions that each heat contains nonmetallic matter of a single and definitely known type. On the basis of such studies the microscopist is able to identify many of the common inclusion types encountered in commercial steels. The application of petrographic and qualitative micro-chemical methods improves the reliability of the identification and increases the variety of types which may be identified.

A paper presented before the Sixteenth Annual Convention of the Society held in New York, October 1 to 5, 1934. This paper is taken from a dissertation submitted by S. F. Urban in partial fulfilment of the requirements for the degree of Doctor of Science at the University of Michigan. Dr. Urban is now associated with the metallurgical department of the National Tube Company at Ellwood City, Pa. Dr. Chipman is research engineer, department of engineering research, University of Michigan, Ann Arbor, Mich. Manuscript received July 2, 1934.

Preparation of Known Oxide Inclusions

Matveieff (1)[1] prepared synthetic inclusions by forging an iron pipe containing known nonmetallic materials. Very pure inclusions were prepared by Wohrman (2). He packed an electrolytic iron crucible with known oxides, placed it in an alundum crucible and melted in an Arsem furnace. This arrangement eliminated most of the objectionable fluxing of the crucible by the inclusions. Herty and his co-workers (3, 4) added deoxidizers to successive ladles of metal from an oxidized bath in an electric furnace. Benedicks and Löfquist (5) have depended upon commercial steels, slags, and minerals. Important microscopic studies of inclusions in commercial steels have recently been reported by Grant (6), Sims and Lillieqvist (7), Zieler (8) and Löfquist (9). For the present study the melts were prepared in a small magnesia-lined induction furnace which was capable of rapidly melting a charge of three or four kilograms. The charge consisted of electrolytic or ingot iron with sufficient iron oxide to saturate the liquid metal. When the melt was thoroughly liquid it was held at temperature for about five minutes, deoxidizer added and the heat cast immediately into a small iron mold. The melting record of heats containing oxide inclusions is shown in Table I.

Table I

Melting Record of Heats Containing Oxide Inclusions

Heat No.	Iron Used	Amount and Type of Deoxidizer Added
1	ingot iron	2.25 per cent ferromanganese
2	electrolytic	3.33 per cent ferromanganese
3	electrolytic	0.16 per cent ferrosilicon (78 per cent)
4	electrolytic	0.27 per cent ferrosilicon
5	ingot iron	0.30 per cent ferrosilicon
6	ingot iron	0.75 per cent ferrosilicon
7	electrolytic	1.00 per cent ferrosilicon
8	electrolytic	1.00 per cent ferrosilicon
9	ingot iron	1.25 per cent silicomanganese
10	electrolytic	1.33 per cent silicomanganese
11	ingot iron	0.30 per cent zirconium-ferrosilicon
12	electrolytic	0.40 per cent zirconium-ferrosilicon
13	ingot iron	0.25 per cent calcium silicide
14	ingot iron	0.25 per cent calcium-silicon-aluminum
15	ingot iron	0.25 per cent aluminum
16	electrolytic	0.33 per cent aluminum
17	electrolytic	0.33 per cent aluminum
18	electrolytic	0.33 per cent aluminum
19	electrolytic	1.66 per cent ferrochromium

The inclusions were studied in the steels in the cast, forged, quenched and annealed conditions. In this study photomicrographs

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

are used to show the various types of inclusions that are formed by different methods of deoxidation. In some cases it is quite impossible to show all that can be seen under the microscope because it is difficult to reproduce color shades. No attempt will be made to describe the few unusual inclusions that were found; the descriptions given apply to the typical inclusions.

Sampling and Polishing

Transverse sections for metallographic studies were cut from each ingot at a height slightly above the center. A segment was cut from each section and polished for examination. The lower half of each ingot was forged to determine the effect of various inclusions on the forging properties of the iron, as well as to determine the effect of forging on the inclusions.

The method of polishing finally adopted was essentially that described by Urban and Schneidewind (10). The modified procedure is as follows:

1. Grinding on coarse and fine emery wheels.
2. Grinding on French emery paper, starting with a number 1 and finishing with a number 000. Numbers 0 to 000, respectively, were coated with stick graphite, which produced a finer finish.
3. Polishing on a billiard cloth disk, using coarse rouge as an abrasive and water as a lubricant.
4. Polishing on a disk covered with a good grade of moistened billiard cloth, which is charged with a fine grade of jeweler's rouge. Water is dropped on the wheel at a constant speed, the water acting as a lubricant.
5. Washing the specimen in benzene and touching up on the same wheel, using only water.

The relative ease or difficulty with which various specimens polish depends largely upon the types of inclusions present in the iron. With the exception of alumina inclusions, most of the specimens can be polished with little difficulty. Alumina inclusions have a marked tendency to wipe, resulting in the formation of a large number of very fine scratches on the area adjacent to the inclusions.

The various types of inclusions resulting from the reaction of dissolved iron oxide with the added elements in the above heats are described in the following paragraphs.

Manganese Oxide-Iron Oxide

Heats 1 and 2. Deoxidized with Ferromanganese. From the similarity in both chemical and physical properties of FeO and MnO it would be expected that the inclusions formed in Heats 1 and 2 would form a simple solid solution. Herty's experimental work (11) on this system indicates a simple solid solution over the entire range of compositions. Wohrman prepared very pure inclusions which consisted of at least two distinct phases. A number of inclusions were found in Heats 1 and 2 that showed the presence of light and dark gray phases but the majority of the inclusions appeared to consist of only one phase. These inclusions were similar to those shown by Wohrman but no photomicrographs are shown here.

Angular but noncrystalline, dark gray inclusions were also found in limited numbers. These inclusions are usually connected by a series of spherical inclusions of the same color. Körber (12) found that the angular type of inclusion is formed when the MnO/FeO ratio is high, while the round type is formed when the ratio is low. All of the inclusions found in these heats showed a marked tendency to elongate upon forging.

Iron Oxide-Silica (Ferrous Silicates)

Heats 3, 4 and 5. Partly Deoxidized with Silicon. A typical inclusion of Heat 3 is shown in Fig. 1. The most striking characteristic of this inclusion is its larger size. The inclusion shown is very typical in that no other type was found in this heat.

In order to gain some notion as to the composition of the phases of the inclusion shown in Fig. 1, inclusions of this type were removed for petrographic-microscopic studies by a method which will be described in detail in a later section of this paper. The dark irregular areas in this inclusion are glassy in appearance and have an index of refraction that is near that of quenched cristobalite. The semi-glassy groundmass, which is very finely dispersed, is a submicroscopic mixture of silica and fayalite. At first thought it may appear strange that cristobalite would be found in inclusions whose total silica content is low. However, Grieg (13) has shown that nearly pure silica will separate rapidly from a less siliceous mass even when the silica content of the latter is low.

Heating to 1000 degrees Cent. (1830 degrees Fahr.) produced

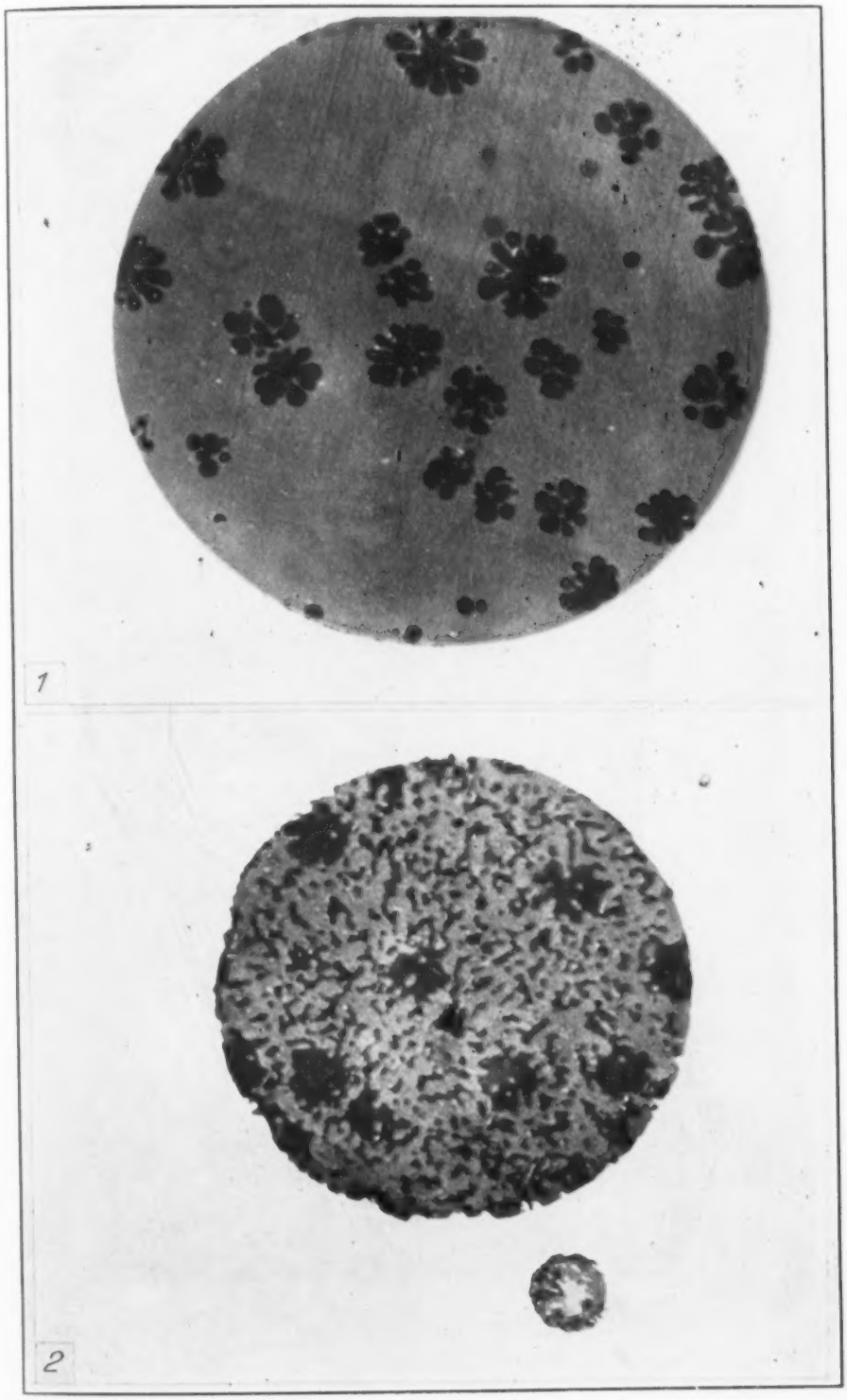

Fig. 1—Ferrous Silicate Inclusion in Heat 3, As-cast; Cristobalite in a Groundmass of Semi-glassy Silicate. × 1000.
Fig. 2—Ferrous Silicate in Heat 3, Annealed. × 1000.

a distinct structural change in these inclusions. Fig. 2 illustrates the change that has occurred on annealing. The silica particles within the inclusions have lost their original outline; however, they are larger and more numerous, indicating a depletion of the less siliceous groundmass. That a depletion of the groundmass has occurred was shown by the fact that it was completely opaque when immersed in the oils used for the refractive index studies.

Since the groundmass of these inclusions is low in silica it would be expected that their melting point should be comparatively low. This was confirmed by the observation that they readily deform on forging as is shown by Fig. 3.

Typical inclusions of Heat 4 are shown in Fig. 4. This heat had an addition of only 0.27 per cent of ferrosilicon, which is an increase of 0.10 per cent over the addition that was made to Heat 3. This rather small increase in the silicon addition was sufficient to effect a change in size and structure, which is shown by comparing Figs. 1 and 4. The majority of the inclusions found in Heat 4 resemble the gray glassy type shown in the photomicrograph; a few of the inclusions were of the semi-glassy type. The "yeast cell" inclusion suggests coalescence; however, it is equally probable that it may represent an arrested stage of subdivision. These inclusions are high in silica, which is indicated by their low indices of refraction.

It is to be noted that the inclusions shown in Fig. 4 have a characteristic series of concentric rings, which are due to reflections of light from the depths of the transparent spherical inclusion. Wohrman (2) suggested that these reflections originate at the surface of a hole from which the inclusion has been torn out during the polishing operation. Even if, as Wohrman suggests, the cohesion between the inclusion and the metal is very weak, it would still be impossible to dislodge an inclusion that had been cut through a plane above its center. As a final proof that the inclusion is actually present, it may be stated that these inclusions could be gouged out under the microscope.

The inclusions in Heat 5 were quite similar to those found in Heat 4; however, they appeared to be more glassy and were definitely smaller, indicating again that the size of the inclusion is partly governed by the amount of silicon added. The more glassy appearance of the inclusion would suggest that they were higher in silica than the inclusion found in Heat 4. However, the indices of refraction of the inclusions in both of these heats are near that of pure quenched

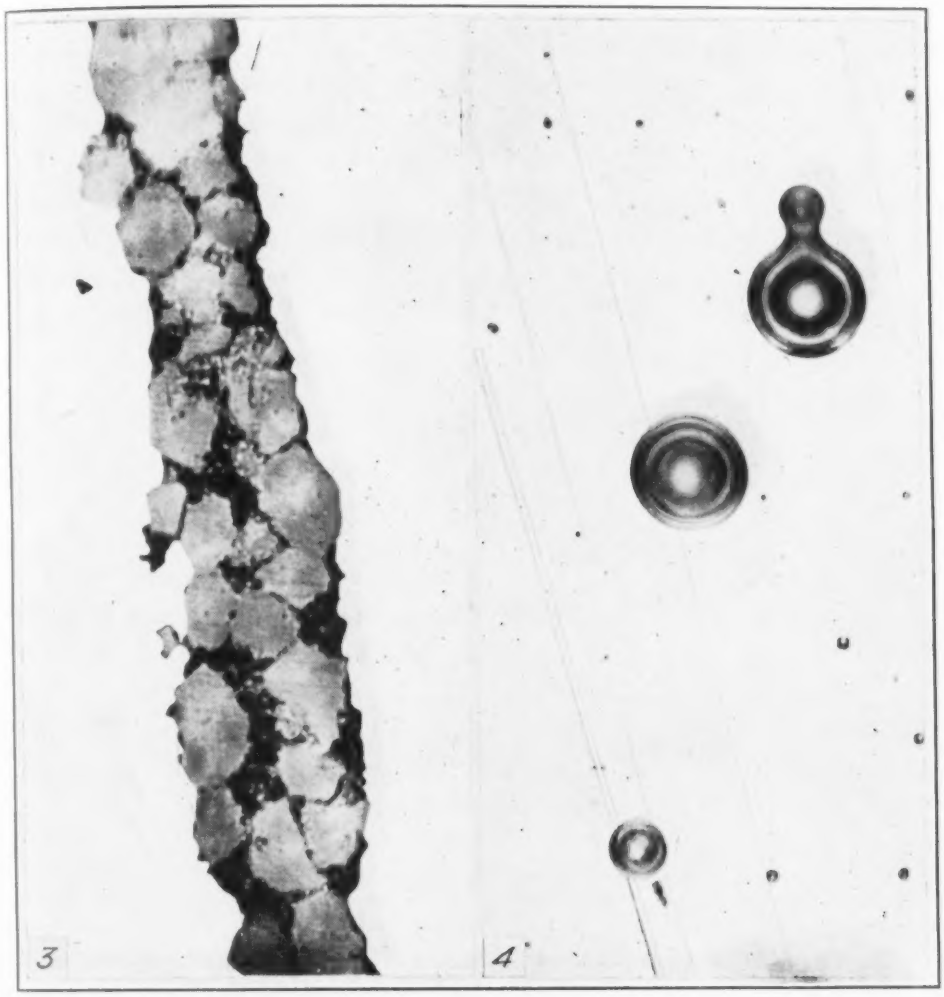

Fig. 3—Ferrous Silicate in Heat 3, Forged. As in the Preceding Photomicrographs the Dark Portions are Cristobalite. × 1000.
Fig. 4—Glassy Silicates in Heat 4, As-cast; Polishing Scratches Indicate Hardness of the High Silica Inclusions. × 1000.

silica. None of the inclusions found in these two heats were affected by either quenching or annealing; however, they were rather easily deformed upon forging.

Heats 6, 7, and 8. Deoxidized with Excess Silicon. Two distinct types of inclusions were found in this series of heats. These are the plain transparent type of inclusions that has been described and the glassy type shown in Fig. 5. The irregular darker areas are similar to the irregular areas shown in the inclusion of Fig. 1, and are pure silica (cristobalite). The groundmass of these inclusions is nearly pure silica, which was checked by their indices. The trans-

parent, silica-rich groundmass produces a rather confusing effect on account of the fact that a number of the pure silica particles are located on various planes below the polished section.

A majority of the inclusions in these heats were slightly affected by quenching and annealing, which produced a slight opalescence. This is a rather interesting situation because we have seen that the low silica inclusions of Heat 1 were markedly affected by either quenching or annealing, while inclusions intermediate in silica (Heats 4 and 5) were not affected. The explanation of this behavior is not evident and should be left open for future study.

Manganese Oxide-Silica. (Manganous Silicates)

Heats 9 and 10. Deoxidized with Silicomanganese. The inclusions in these heats could readily be mistaken for those shown in Fig. 5. They contained pure silica embedded in a semi-glassy to glassy groundmass. The index of refraction of this groundmass is much higher than that of ferrous silicates rich in silica and is very near that of rhodonite ($MnO \cdot SiO_2$). The large size of these inclusions indicates that they would be eliminated from the steel bath with comparative ease. Herty and co-workers (14) have found this to be true of heats deoxidized with silico-manganese alloys.

Zirconium-Ferrous Silicate

Heats 11 and 12. Deoxidized with Zirconium Ferrosilicon. All of the inclusions found in these heats were complex in structure; they all showed a green tinge which is characteristic of zirconium silicates. Deoxidation with an alloy containing zirconium would suggest the possibility of forming zirconia (ZrO_2) inclusions, which would be crystalline because the melting point of zirconia is much higher than of iron. These were conspicuous by their absence. Similarly, it may be said that the inclusions are not zircon ($ZrO_2 \cdot SiO_2$), nor the eutectic of zircon and zirconia because these also have very high melting points. This leaves only one possibility, namely, that the inclusions formed in these two heats consist of zircon fluxed with either ferrous oxide or ferrous silicates, and would, therefore, be liquid at steel melting temperatures which is indicated by the fact that the inclusions were readily elongated on forging. An example of a large zirconium-ferrous silicate inclusion which has been elon-

Fig. 5—Glassy Silicates Containing Cristobalite in Heat 8, As-cast. × 1000.
Fig. 6—Zirconium-ferrous Silicates in Heat 12, Forged; Showing the Tip of a Large Elongated Inclusion. × 1000.

gated in forging is shown in Fig. 6. This inclusion was unusually large and only one end of it is shown in the photomicrograph.

Complex Silicates

Heat 13. Deoxidized with Calcium Silicide. Heat 14. Deoxidized with Calcium-Silicon-Aluminum. The inclusions found in these heats were quite complex, showing as many as three phases, although a number of glassy inclusions were found that were rich in silica and had the same index of refraction as the ferrous silicates high in silica. These glassy inclusions were readily devitrified on annealing. Since the inclusions are so complex in structure it is quite hopeless to try to identify the various phases, however, it may be stated that no free calcium ferrites were found and none of the recognized compounds of the lime-alumina-silica system. The typical inclusions of these heats showed a decided tendency to elongate on forging, indicating that their melting points are below that of liquid steel.

Observations in Polarized Light

When an anisotropic substance is observed in polarized light with the Nicol prisms crossed, the intensity of the reflected or transmitted light depends upon the orientation of the substance relative to the plane of polarization of the light. In the ore microscope used in this study, light passes through the polarizing prism to the specimen from which it is reflected through the analyzing prism to the eyepiece. If the orientation of the specimen is altered by rotating the stage of the microscope, the light intensity varies through successive maxima and minima. When an isotropic crystal is observed with the prisms crossed the intensity of the light is very low and is unaffected by the orientation of the specimen. It is thus possible to distinguish between inclusions which are isotropic and those which are anisotropic without removing them from the steel specimen in which they are found. This method has proven especially useful in the identification of certain sulphides and of the oxides described in the following paragraphs. It is also useful on occasions for distinguishing between sulphides and silicates in rolled or forged specimens. The latter appear brilliantly illuminated against a dark background when examined under crossed Nicols.

Alumina and Aluminates

Heats 15, 16, 17, and 18. Deoxidized with Aluminum. The inclusions in these heats are particularly interesting because they have been the subject of numerous discussions. In 1915 Comstock (15) showed by photomicrographs the inclusions that are formed when a bath is deoxidized with aluminum. He described the inclusions as being very small and very difficult to polish, showing a marked tendency to segregate into groups which formed stringers when the steel was forged. Recent studies have not added materially to the description given by Comstock, which may be partly accounted for by the fact that a number of inclusion types are formed under very similar conditions.

In Fig. 7 is shown a typical group of inclusions that were found in Heats 15 and 16. The dark angular inclusion at the top of the photomicrograph was quite rare for these heats, while the irregular groups in the central portion of the photomicrograph are most typical. The irregular groups are very difficult to polish without the formation of "comet tail" scratches, a few of which are still visible even though extreme care had been exercised in preparing the specimen. Numerous investigators have called the irregular dark areas alumina; this is believed to be in error, since alumina should be translucent. The light particle that is embedded in the dark mass may be alumina because under the microscope it is nearly transparent.

Figs. 8 and 9 show the various types of inclusions that were found in ingot 18, which was not dead killed and showed a slight porosity. The gray inclusions shown in Fig. 8 were found near the skin of the ingot. They are ferrous aluminate in various stages of fluxing with the excess ferrous oxide that was present. The inclusions found in the center of the ingot are shown in Fig. 9. Examination in polarized light discloses the fact that the crystals are isotropic and, therefore, not corundum, which is hexagonal. They appear to belong to the cubic system, even in the case of the one crystal whose outline is hexagonal. Now if an iron-alumina spinel were formed, it would be a cubic crystal of the composition $FeO \cdot Al_2O_3$. Such a compound might reasonably be expected, but the work of Herty and his associates (4) on the system ferrous oxide-alumina shows no such compound and indicates that a mixture corresponding to this composition has a melting point considerably below the temperature at which these crystals were formed.

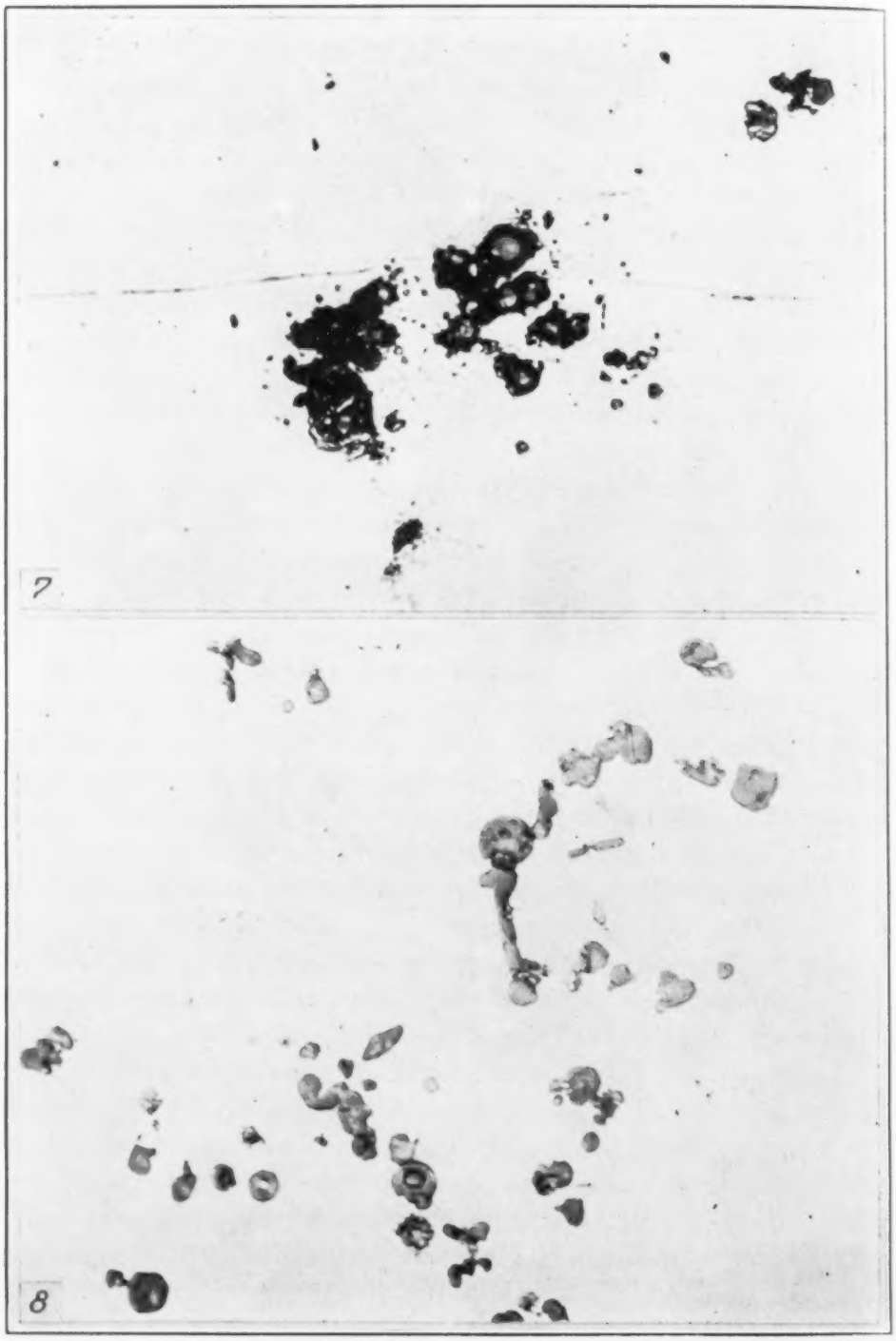

Fig. 7—Typical Inclusions in Heat 15 Deoxidized with Aluminum. × 1000.
Fig. 8—Ferrous Aluminate Inclusion Fluxed with Excess Ferrous Oxide, Heat 18, As-cast. × 1000.

The best we can do at the present time, therefore, is to call these inclusions ferrous aluminate and leave to future research the task of determining their exact nature.

None of the inclusions found in any of the heats deoxidized with aluminum showed any structural change on quenching, annealing, or forging, indicating that all of the inclusions have a rather high softening temperature; for we have seen that oxide inclusions that have a comparatively low melting point are affected by these operations.

Chromic Oxide-Iron Oxide. (Chromite)

Heat 19. Deoxidized with Ferrochromium. Fig. 10 shows the only type of inclusion that was found in this heat. These inclusions are characterized by their purple color and angular form, which is in agreement with the description given by Comstock (15). The crystallinity of these inclusions indicates that their melting point is above that of iron. The same type of inclusions were found in ferrochromium and in chromium steels. As would be expected they are not affected by either quenching or annealing. Since these inclusions have a tendency to segregate into groups like alumina inclusions, they form stringers on forging, although the individual inclusions are not deformed.

Previous investigators have invariably called these inclusions chromic oxide. An examination of Fig. 10 reveals that the inclusions are cubic sections. When examined in polarized light by the method described above they are found to be isotropic. They are, therefore, not chromic oxide, which is hexagonal, but chromite ($FeO \cdot Cr_2O_3$), which is cubic.

Petrographic Examination of Silicate Inclusions

The determination of the optical properties of a transparent or translucent substance is not a tedious process once the proper technique is acquired. The methods have been developed by petrographers and are among the most important tools of the mineralogist.

Hartmann (16) studied large inclusions with the aid of polarized light. These inclusions were readily visible to the unaided eye, most of them being stringers which were removed from forged or rolled steels and were about two inches in length and three to five

Fig. 9—Ferrous Aluminate Inclusions (Crystals) Held Together by a Material Whose Nature is as Yet Unknown. Heat 18, As-cast, × 1000.
Fig. 10—Chromite Inclusions in Heat 19, As-cast. × 1000.

hundredths of an inch in width. It is evident that inclusions of this size are rare and that Hartmann's technique would not be very useful for the study of ordinary inclusions. From a piece of steel in which an inclusion was embedded Hartmann machined a small plate or rod, containing the inclusion. The separation of the iron was accomplished by the use of chlorine. The steel containing the inclusion was heated at 500-600 degrees Cent. (930-1110 degrees Fahr.) in a chlorine atmosphere, the iron being volatilized as ferric chloride. The residue was then heated in a muffle to remove the carbon. If the inclusion was sufficiently large a thin section was prepared, but if the particles were small or had been obtained by scraping, they were mounted in Canada balsam, sectioned and polished in the usual manner. The identification was made by comparing the slide containing the unknown inclusion with slides of known nonmetallic substances.

The following technique has been developed for the removal of small inclusions and their petrographic examination. In order to be able to remove any particular inclusion that may be of interest for study it is necessary to have a proper tool. This is made by mounting a fine steel needle in the barrel of a watchmaker's screw driver. The needle point appears to be quite large under the microscope; it is, therefore, necessary to grind the needle to an extremely fine point. A specimen is now examined under the microscope and small circles are drawn around a number of the inclusions that appear to be of the same structure. The inclusions are removed by forcing the needle vertically into the steel at a point near the inclusion. By holding the needle point in the hole formed it is a simple matter to dislodge the inclusion by moving the free end of the needle downwards. If the needle is now moistened with oil the inclusion can be picked up and transferred to a slide on which a drop of the oil (of known index) has been placed.

When a substance immersed in oil is observed under the microscope, a band of light appears at the interface between the oil and the substance. As the tube of the microscope is raised this light band (the Becke line) always shifts across the interface in the direction of the substance of higher index. The index of refraction of the extracted inclusion is determined by immersing it in liquids of known indices and noting the movement of the Becke line. The operation is repeated with different liquids until one is found with an index equal to that of the substance at which point the Becke line dis-

appears. This method was found to be especially useful for the silicate inclusions that were not differentiated by the microchemical methods which will be described later.

Ferrous Silicates. The inclusions in Heat 3 are gray in color and of the semi-glassy type. The irregular areas shown in the inclusions (Figs. 1 and 3) have an index of 1.47 which is very close to that of quenched cristobalite. The index of the groundmass is somewhat greater than 1.74, indicating that it is very low in silica. The quenched and annealed specimens were not suitable for studies because the inclusions were nearly opaque.

The refractive indices of the inclusions in the five heats deoxidized with ferrosilicon are given below. Indices were determined in the cast, quenched, and annealed states, the two latter being indistinguishable.

Heat No.	Type	Index of Refraction		Remarks
		As Cast	Annealed	
3	Figs.1 and 3 (ground mass)	1.74	at 1000° Cent. opaque	Low silica
3	Fig. 1 (Precipitated particles)	1.47	....	Cristobalite
4 and 5	Fig. 4 Glassy	1.47-1.50	1.47-1.50	Silica Glass
6	Glassy	1.53	1.55	Ferrous silicate glass
7	Glassy	1.50	1.50	Ferrous silicate glass
8	Glassy	1.50	1.50-1.52	Ferrous silicate glass

The increase in refractive index in Heats 6 and 8 on heat treatment denotes an increase in the ferrous oxide content of the glass. This was indubitably the result of a precipitation of silica, probably as cristobalite, which was further evidenced by a slight opalescence after annealing. The same devitrification was observed in Heat 3 as shown in Fig. 2. In this case, however, the inclusion after heat treatment was too opaque for a determination of its index.

Manganese Silicates. Most of the inclusions in Heats 9 and 10 contained irregular patches whose index was close to 1.49, indicating that these portions are nearly pure silica. The groundmass of the inclusions had an index close to 1.72. The indices of refraction of rhodonite ($MnO \cdot SiO_2$) and tephroite ($2MnO \cdot SiO_2$) are close to 1.73 and 1.78 respectively. Ferrous silicates of an index of refraction of 1.72 would be nearly opaque and, since the inclusions in this heat are glassy, it is apparent that they are manganese silicates, probably containing rhodonite. Annealing

completely changed the structure of the inclusions and the index of refraction was greater than 1.74, which was the limiting value for the oils available. The complex silicate inclusions in Heats 11, 12, 13, and 14 were not suitable for studies because all of them were opaque.

Summary

A series of melts was deoxidized with various elements in order to study the types of inclusions formed. The inclusions studied are nearly pure oxides. All of the inclusions were examined in the steels in the cast, quenched, annealed and forged conditions. A limited number of inclusions were affected by quenching or annealing. These were ferrous silicates low in silica and manganese silicate inclusions. Aluminate and chromite inclusions were not affected by any of the treatments.

Small additions of silicon will produce ferrous silicate inclusions, while larger additions of silicon produce inclusions that are nearly pure silica. Segregated portions of pure silica are found in highly fluxed inclusions whose total silica content is low. It has been further shown that precipitation of silica within these inclusions occurs at 1000 degrees Cent. (1830 degrees Fahr.).

From studies in polarized light it is concluded that the inclusions formed when chromium is added to a steel bath are chromite and not chromic oxide. Similarly it is found that in steels deoxidized with aluminum the inclusions are ferrous aluminates whose exact composition cannot be stated with certainty.

A method for the removal of individual small inclusions has been developed and a petrographic method has been suggested for the classification of silicate inclusions. The method is both rapid and accurate and is not open to the objections that are common to chemical methods.

Acknowledgments

The authors wish to express their thanks to Professor A. B. Peck of the Department of Mineralogy for his valued assistance and advice, and to the Timken Steel and Tube Co., under whose sponsorship this investigation was begun.

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DISCUSSION

Written Discussion: By C. E. Sims, research metallurgist, American Steel Foundries, Indiana Harbor, Indiana.

It seems that the authors have made a fine start in the right direction to increase our fundamental knowledge of nonmetallic inclusions. Only by knowing the simpler types can we hope to understand the more complex ones. But as shown here, even the simplest conditions give rather complex inclusions.

One of the most valuable contributions of this paper is the confirmation of the apparent fact that deoxidizers, even the most powerful such as aluminum, do not completely reduce the FeO present in steel. This indicates the relatively great importance of the laws of mass action as compared to stoichiometric proportions in the reactions of steel-making.

Written Discussion: By Neil Metcalf, metallurgist, Treadwell Engineering Co., Easton, Pennsylvania.

The authors spoke about the condition of the melts, or rather the deoxidation products of these melts.

I am interested in knowing the condition of the melts before deoxidation. For instance, if one is making say a 0.30 to 0.40 per cent carbon steel, different results would be obtained, depending upon whether the melt down was made without adding ore, or whether ore was added, with subsequent boiling down to possibly 0.10 per cent carbon, followed by pigging back.

In the latter case the oxidation products formed during the melting have a better chance of rising and being out of the steel before adding the deoxidizers. A different type of deoxidation product would be expected in each case.

This raises the question as to whether the primary oxidation products are not responsible for more trouble than the deoxidation products formed by the addition of deoxidizers. And with this in mind, whether the method of working the bath is not more important than the type of deoxidizer used, having reference to the cleanliness of the steel produced.

Oral Discussion

DR. C. H. HERTY[1]: I am going to take this opportunity to inject a few words on the condition of the metal before deoxidation. In 1926 we began to study deoxidation with silicon, and one of the first things we went after was the type of inclusions formed when silicon was added to oxidized metal. We wanted to find out all we could about the different silicates, and we made an open-hearth heat in a small electric furnace, getting the carbon way down so we would have plenty of iron oxide to react with the silicon and aluminum, and manganese, or whatever we used. The intent was to get as many inclusions as we could so as to study the physical properties of the inclusions. I always felt that we should have taken another series where the iron oxide content corresponded to a spring steel; we should have made at least three different tests, where we had highly oxidized metal in one, medium in another, and the third with very little iron oxide in it, because what you get of course depends on the ratio of the deoxidizer added to the iron oxide present at the time of the addition, and while you can similate that to some extent by raising the deoxidizer higher than you would in practice, still that does not always tell you the story, and we have found when we began to make hundred-ton heats that we had overlooked a very good bet in not throwing into our experiments at least a few ingots which were made from 0.15 to 0.20 per cent FeO metal instead of 0.40 to 0.45 per cent FeO metal. I was going to bring that up and I personally hope that in Dr. Chipman's continuance of this work he will take advantage of the mistake we made to at least try to vary the iron oxide as well as the amount of deoxidizer added, because I think it will enable us to take a good many short cuts when we begin to work with these deoxidizers in practice.

I think this type of paper where we are studying fundamentally iron oxide and a single or double deoxidizer is intensely valuable. When we have built up an entire system of all the available deoxidizers and any new ones that we happen to have, we will really have a ground work on which to base our work. I know that our silicon work in the laboratory was of the greatest help when we began to study silicon in the open-hearth, and on these other deoxidizers such as titanium, we should have the fundamental data on the deoxidizing reactions, which Chipman presented last fall, and the kind of deoxidation products obtained. Until we do get all the knowledge of those different systems we are going to have to cut and try in steel making just as they did in the early work of the Bessemer process.

DR. JOHN CHIPMAN: In answer to the question and remarks, I will say that no one realizes more fully than Dr. Urban and myself the incompleteness

[1]Metallurgical Division, Bethlehem Steel Co., Bethlehem, Pa.

of the work which is described. The fact that it is so incomplete is not due so much to our desire to skim over it or touch it lightly, but to the fact that if one were to make a complete study of such things, such a study might run into an exceedingly long period of years. Certainly there is a difference between inclusions formed by the sudden deoxidation of a highly oxidized bath and those inclusions which are formed in a final deoxidation of a bath whose oxygen content has already been substantially reduced. This difference we have not taken into account in the present work, as all of our specimens were formed by the addition of the deoxidizers to quite highly oxidized iron. That is to say, the iron which was melted in an induction furnace was treated to increase its oxygen content and then the deoxidizer was added. We were doing exactly what Dr. Herty had done, striving to get an ingot that was just full of inclusions, and we did.

Dr. Urban has prepared two or three more parts of this general study of inclusions and we hope to be able to report on sulphide inclusions, oxide and sulphide inclusions, nitride inclusions, and on chemical etching methods for identification of the simpler types of inclusions, following up the work so admirably begun by Comstock, Wohrman and others.

THE EFFECT OF DEOXIDATION ON SOME PROPERTIES OF STEEL

By C. H. Herty, Jr.

Abstract

Many of the present day specifications for steel parts are concerned with qualities which are controlled to a large extent by the method of deoxidation used during the manufacture of the steel, and not by its ordinary chemical analysis. This paper indicates some of the variations in the physical make up of the steel as affected by the method of deoxidation and gives specific examples to show the effect of these variations on some of the properties of the product. Grain-size, hardenability, aging and impact strength at low temperatures are used as illustrations.

IN 1926, various companies in the steel industry, represented by a Metallurgical Advisory Board, began a co-operative project with the Carnegie Institute of Technology and the United States Bureau of Mines on the general subject of the "Physical Chemistry of Steel Making." The work was financed jointly by all three co-operating parties and its primary object was to obtain data on the chemical reactions which take place in the manufacture of steel and to study the effect of the chemical and physical reactions involved in the behavior of the finished product. On December 31, 1931, the Bureau of Mines withdrew from the project and the other parties continued the work.

At the outset, the research program divided itself into two main lines. First; laboratory experiments for the determination of certain necessary chemical constants involving solubility of materials in liquid iron, melting points of various slag systems and physical characteristics of inclusion-forming materials. Second; experimental heats in open-hearth furnaces where results from the laboratory were translated into practical terms as rapidly as possible. These two methods of attack were very easy to carry out simultaneously as the Bureau of Mines had as part of its equipment an excellent

A paper presented before the Sixteenth Annual Convention of the Society held in New York City, October 1 to 5, 1934. The author, C. H. Herty, Jr., at the time this paper was written was Director of Research, Metallurgical Advisory Board to Carnegie Institute of Technology, Pittsburgh. He is now associated with the metallurgical division of the Bethlehem Steel Co. Manuscript received June 29, 1934.

electric furnace laboratory with various furnaces ranging in capacity from a few grams up to three hundred pounds and there were in the Pittsburgh District open-hearth furnaces of almost any size and almost every kind in which experimental work could be carried out. The experimental work has been concentrated on the open-hearth process and the following discussion refers to this steel-making operation. The results of the investigations have been published from time to time as Co-operative Bulletins of the Carnegie Institute of Technology, as Bureau of Mines Technical Papers and in the Technical Press.

To any consumer of steel the major interest in such a program must necessarily be in the results of the steel-making process on the properties of the product rather than in the technical details of the process itself. It is, however, impossible to discuss the first without some reference to the second and a very brief summary of the steel-making process as we see it today should precede the discussion of the product in this paper.

In order for the producer of steel to meet the ordinary chemical specifications of the product it is necessary to perform a drastic oxidation of the metal. Such oxidation, carried out by means of suitable slags, causes a partial elimination of carbon, manganese and phosphorus and an essentially complete elimination of silicon from the pig iron and scrap charged. At the time that the carbon and phosphorus are eliminated to the desired degree the metal contains dissolved iron oxide, the amount dependent upon a number of physical and chemical factors.

In order to meet the chemical specifications and to make an ingot from which a given product may be rolled with the minimum loss of metal, deoxidizers are added to the liquid steel, and the iron oxide content of the metal is reduced to an extent dependent on the amount and strength of the deoxidizers added. When these deoxidizers are added to the liquid metal their reaction with iron oxide results in the formation of tiny particles of nonmetallic matter, some of which have a slight but positive solubility in the liquid iron, whereas others are essentially insoluble. With these facts in mind, we must consider the metal entering the mold as containing iron oxide in solution, other oxides in solution, oxides in suspension, (and it should be mentioned here that the particles that make up these suspensions vary in size from those which are colloidal in nature to those which are large enough to actually float out of the steel) and

alloying elements to meet the chemical specifications. During the solidification period, some of the soluble materials become insoluble either through a change in solubility, resulting from a lowering of the temperature, or by chemical reaction. At the same time some of the particles of the fine suspensions may either agglomerate or coalesce with the formation of larger inclusions, these being the basis for most of the particles seen when the finished steel is examined under the microscope.

The laboratory studies mentioned previously were designed to determine the chemical reactions and physical constants involved in the steel-making process as described in the last paragraph. Among the more important projects were first; the determination of the solubility of iron oxide in liquid iron over a wide temperature range, and the development of methods for the determination of iron oxide in liquid steel; second; the determination of the melting point and relative fluidity of the slags which are formed from deoxidation products; third; the development of special deoxidizers following a comprehensive study of the common deoxidizers. In this work it was, of course, necessary to include an extensive study of analytical methods.

The effect of change in chemical composition on certain physical properties has been widely studied from the earliest days of steel making. Such studies have led to a host of new products and most of the common effects of alloying elements are fairly well understood. It is only recently, however, that the effect of the steel-making process itself has begun to be investigated quantitatively. That steels of the same chemical composition occasionally show widely varying properties has been known for a long time. The steel melter used the general term "body" to indicate that certain steels or heats of steel would give physical results which could not be obtained by other steels of the same grade. During the period when "dirty steel" was the fad, much of the variation in properties of steels was attributed to visible nonmetallic inclusions and there are good grounds to believe that in certain instances this has been true.[1] Graham[2] recently discussed steel quality from the standpoint of variations in the steel-making process with reference to those elements which are not usually shown by the ordinary chemical analysis. Most of the papers of the

[1]H. E. Howarth, "Greenish Colored Markings in Steel Test Pieces," *Journal*, Iron and Steel Institute, No. 2, 1905, p. 30.

[2]H. W. Graham, American Iron and Steel Institute Yearbook, 1932, p. 59-114.

past decade on the properties of steel have omitted the deoxidation of steel as a variable.

Going back to the concept of the condition of the steel entering the mold and the reactions which take place during solidification, it will be noted particularly that aside from chemical composition there are nonmetallic elements in solution and in suspension and that the amounts of material in solution and the type of suspension are due largely to the deoxidation methods employed. Let us consider a few of the properties of steel which might be affected by these solution and suspensions.

Grain Size

It is the general concept at this time that fine-grained steels are the result of the presence of a fine suspension which furnishes nuclei for recrystallization during heating through the critical range. Steels of the same grade will vary in grain-size as a result of the type of fine suspension present. For example, if a steel is deoxidized with silicon alone it will always tend to be coarse-grained and will show a marked coarsening of grain when overheated. Aluminum-killed steels, on the other hand, are almost always fine-grained and will not coarsen until a higher overheating temperature is applied than was the case in the original coarse-grained steel. This is illustrated in Fig. 1, which shows a 0.19 per cent carbon silicon-killed steel and a 0.15 per cent carbon aluminum-killed steel in the normalized and overheated condition. Steel AX (silicon-killed) tends to be coarse-grained in the normalized condition and exhibits a marked grain growth when held at 1000 degrees Cent. (1830 degrees Fahr.) for ½ hour. Steel SMA-15 (aluminum-killed) is very fine-grained in the normalized condition and shows very little grain growth when overheated to the same extent as AX. In this instance we have a variation in type of suspension causing a marked difference in a physical property of the steel and it might be emphasized that large variations in grain size may be obtained by the manipulation of deoxidizers to give various types of suspensions.

Rates of Transformation

In low and medium carbon steels it has been shown[3] that the rate at which ferrite is formed during the transformation of γ to α iron is proportional to the grain area per unit of volume and

[3]Reports to the Metallurgical Advisory Board, October, 1933.

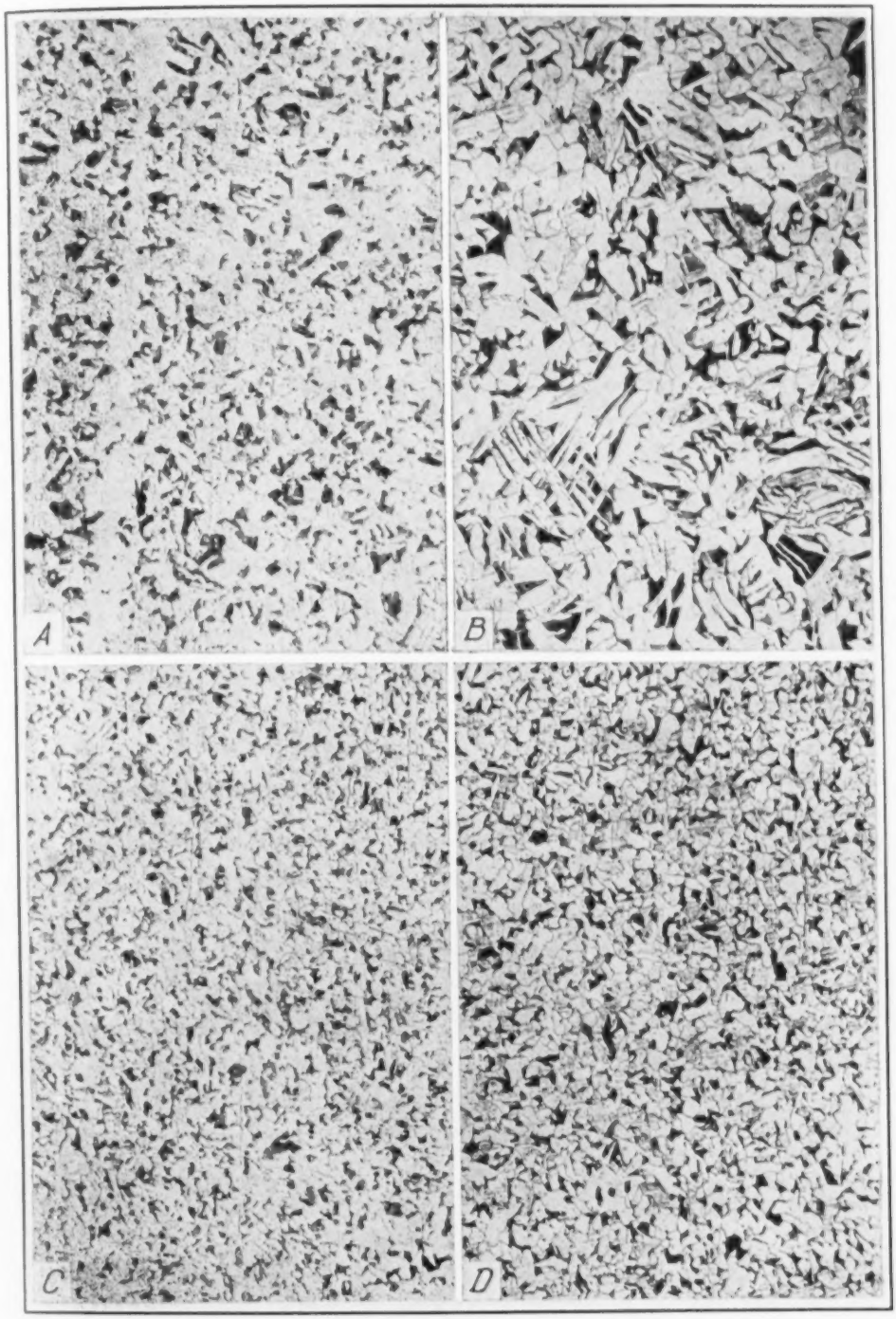

Fig. 1—Effect of Deoxidation on Grain-Size and Grain Growth in Mild Steels:
A—Silicon-killed Steel AX, Heated to 875 Degrees Cent. for ½ Hour—Air Cooled.
B—Silicon-killed Steel AX, Heated to 1000 Degrees Cent. for ½ Hour—Air Cooled.
C—Aluminum-killed Steel SMA-15, Heated to 875 Degrees Cent. for ½ Hour—Air Cooled.
D—Aluminum-killed Steel SMA-15, Heated to 1000 Degrees Cent. for ½ Hour—Air Cooled. All micrographs at × 100.

to the specific reactivity of the steel. Fine-grained steels obviously transform more rapidly than coarse-grained steels on account of the larger grain surface involved. However, if both fine- and coarse-grained steels be overheated until they both have the same grain-size, the steel which was originally fine-grained will still have a higher transformation rate than the originally coarse-grained steel. This higher transformation rate is presumably due to the presence of fine particles which act as nuclei for ferrite formation. In this particular instance the specific reactivity is not as great a factor in rate of transformation as is grain-size, but the effect is nevertheless present and would undoubtedly cause some variations in certain properties which depend on the extent to which the transformation occurs. This subject of rate of transformation and specific reactivity is of the utmost importance in all heat treatments. In hardened steels for example, the two factors, grain-size and specific reactivity determine, for a given quenching procedure, the depth of hardening and the properties of the hardened piece. In this connection, the work of Bain[4] should be mentioned, as it has been of extreme importance in showing how grain-size and alloying elements affect the rate of transformation of a steel.

Impact Strength at Room Temperature

In an investigation of the transverse impact strength of plain carbon steels[5] it was found that the impact strength is proportional to the amount and composition of ferrite present. The amount of ferrite present was a function of the grain-size and the specific reactivity and therefore directly influenced by deoxidation methods. Certain factors such as banding and large nonmetallic inclusions were shown to cause a lowering of the impact value for a given amount and composition of ferrite and both these disturbing factors are of course traceable with certainty to the manufacture of the steel.

Impact Strength at Low Temperatures

Of considerable interest at this time is the question of low temperature impact strength of steels. There have recently been

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[4]E. C. Bain, "On the Rate of Reactions in Solid Steel," Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, Vol. 100, 1932, p. 13.

[5]M. W. Lightner and C. H. Herty, Jr., "Transverse Impact Strength of Plain Carbon Normalized Steels," Cooperative Bulletin No. 59, Carnegie Institute of Technology and the Metallurgical Advisory Board, 1932.

published a number of articles dealing with the low temperature impact properties of alloy steels. To illustrate the effect of deoxidation on the low temperature impact properties of plain carbon steels, Table I has been prepared from an extensive investigation on this subject, the material to be published in full later in the year. The four steels were made as follows: Steel 1, a rimmed steel deoxidized with manganese only. Steel 2, a silicon-killed steel deoxidized with manganese and silicon, (Steel AX of Fig. 1). Steel 3, a so-called semi-killed steel, deoxidized with manganese and a small amount of silicon and aluminum in the ladle. Steel 4, a dead killed steel strongly deoxidized with silico-manganese, (this material having been developed in the laboratory work referred to previously) followed by deoxidation with an excess of aluminum, (Steel SMA-15 of Fig. 1). The dissolved oxygen content of these ingots decreases with the order of the steels above. The impact tests were Charpy tests with an Izod notch as specified by the B. E. S. A. and the A. S. T. M.

Table I
Low Temperature Impact Strength of Plain Carbon Steels

Charpy Impact Test with Izod Notch

Steel No.	Testing Temperatures +75 Degrees Fahr.	−40 Degrees Fahr.
1	44.0	2.0
2	74.0	7.5
3	105.0	19.0
4	145.0	110.0

Chemical Composition

Steel No.	C	Mn	P	S	Si	Al
1	0.14	0.51	0.021	0.035	Nil	Nil
2	0.19	0.43	0.023	0.041	0.152	Nil
3	0.15	0.56	0.024	0.040	0.074	0.010
4	0.15	0.71	0.011	0.029	0.074	0.030

In this instance the effect of deoxidation is very pronounced. The temperature at which the more rapid lowering of the impact value occurs decreases considerably with decreasing iron oxide content of the steel. It has been shown in numerous instances that certain alloying elements, such as nickel, lower this temperature, and it is highly probable that by combining the proper alloying elements with the proper steel-making process unusually good properties at low temperature might be anticipated.

Aging Characteristics

A very important property of steels is their change in physical properties after low temperature heat treatments or after cold deformation. Certain types of steel embrittle readily following cold work while others retain to a large degree their original ductility. Using as an illustration the four steels listed in the section above, the effect of deoxidation can be readily seen by an example of quench aging and one of strain aging. For quench aging the steels were quenched in oil from just below the lower critical and allowed to age at 30 degrees Cent. for two weeks. The Rockwell "B" hardness was taken immediately after quenching and at the end of the aging treatment. For the strain aging the steels were normalized and then compressed 15 per cent, heated to 450 degrees Cent. for five minutes and held at room temperature for one day. Izod impact tests were made on these steels before and after the aging treatment. Table II shows the results of these two of aging treatments.

Table II
Effect of Deoxidation on Aging of Carbon Steels

Steel No.	Increase in Hardness (Rockwell B) After Quenching	Izod Impact—Foot-Pounds Before Strain Aging	Izod Impact—Foot-Pounds After Strain Aging
1	9.9	54.2	6.2
2	7.2	72.5	14.4
3	4.6	77.5	22.9
4	2.1	85.3	75.3

It will be noted that the change in hardness after quenching was the greatest in the steel which gave the greatest drop in impact after the strain aging and that the two sets of data are in every instance consistent with respect to the two properties. Furthermore, it will be noted that the order of resistance to aging is the same as the order of resistance to low temperature embrittlement. In this connection, Epstein[6] showed very strikingly the relative embrittlement of steels containing variable amounts of nitrogen which were the direct result of the steel-making process employed.

The above illustrations show very clearly that for a given chemical composition, widely varying properties may be obtained by a variation in the method of manufacture of the steel and the steel maker of today is very much alive to this phase of the steel-making problem. The steel industry has invested $130,000.00 in the work

[6]S. Epstein, "A Study of the Embrittlement of Hot Galvanized Structural Steel," *Proceedings*, American Society for Testing Materials, Vol. 32, Part 2, 1932.

of the Metallurgical Advisory Board, aside from the cost to the various plants in which the experimental work has been conducted. A great deal of money is being spent in various committees with consumers on numerous problems related to special properties such as creep, fatigue, etc., and in these problems the effect of the steel-making process is being investigated. The important factor, oxidation of the metal, is not yet completely under control, but much progress has been made along these lines in the past three years and the results obtained show the rapid strides by which the steel maker is approaching the solution of many of the problems with which both producer and consumer have been confronted in recent years. Furthermore, it may be expected that with the information now being accumulated a much more intelligent attack on new problems may be anticipated.

DISCUSSION

Written Discussion: By H. W. Graham, general metallurgist, Jones and Laughlin Steel Corp., Pittsburgh.

In this short paper Dr. Herty has, as usual, made a contribution of value. The value in this case rests in the fact that the information presented is rationally in line with the conceptions which must govern steel-making methods as applied to the manufacture of a product of specific and intended quality. It is a most promising sign that metallurgists generally are proceeding in a constructive way to link the theory and practice of steel-making with the processing requirements of fabrication and with the ultimate demands of conditions in use.

The detailed data presented by Dr. Herty in this case point out the marked effect of strong deoxidation with aluminum. In considering the attainment of a fine grain structure by the use of rather considerable quantities of aluminum, it is of both practical and technical interest to bear the following situation in mind: A given combination of raw materials and steel-making methods tends to produce a natural level of grain-size and physical behavior characteristics, and it would be a mistake to think that two heats are in all respects alike wherein the same grain-size is attained if there is an appreciable difference in the amount of aluminum or other element which must be used.

In other words there is in grain-size the same situation of "residual" and "added" effects which have long been recognized in the use of phosphorus and sulphur. The effect is sensibly different if it is wholly or largely residual as compared to those cases where it is largely added. This comment merely goes to show what an intricate and complex business steel-making really is, and to indicate that equality of grain-size or even grain growth characteristics does not necessarily mean absolute parity of all phases of quality.

Written Discussion: By John Chipman, Department of Engineering Research, University of Michigan, Ann Arbor, Michigan.

Steel makers should be grateful to Dr. Herty for this clear and concise

demonstration of the marked effect which the method of deoxidation exerts upon the properties of the finished steel. This is one of the most interesting of the many practical results which have come out of this nicely balanced program of theoretical and practical research.

Steel No. 4, otherwise designated SMA-15, is especially interesting as it typifies the results of the silico-manganese-aluminum deoxidation practice developed by Herty and his co-workers. The completeness of the deoxidation of this heat may be judged from the following considerations. According to the deoxidation diagram for aluminum reported a year ago, the equilibrium concentration of iron oxide after deoxidation is calculated to be below 0.002 per cent. I have analyzed several specimens from this heat by vacuum fusion at 1650 degrees Cent. (3000 degrees Fahr.) and have found 0.0013 per cent oxygen, the lowest percentage I have ever observed in a low carbon steel. A large part of this is accounted for as alumina inclusions so that the oxygen present as FeO is certainly far below 0.001 per cent and the FeO, therefore, below 0.004 per cent. A fractional analysis was conducted by the Reeves' method at 1100 degrees Cent., which is supposed to give the oxygen present as FeO. The result of this analysis indicated that the concentration of iron oxide was so low as to be undetectable. As little as 0.002 per cent FeO could readily have been detected.

Dr. Herty is to be congratulated upon the development of a deoxidation practice which really deoxidizes.

Oral Discussion

J. W. KINEAR:[1] Dr. Herty, I would like to ask whether, in your work on increased deoxidation, you have noticed any trend toward increasing sensitivity in medium, high carbon or alloy steels of large cross sections? By this I mean steels that in subsequent rolling, forging or heat treatment have more strains set up than in the former more sluggish steels of the same chemical composition. May we not, by increasing the speed of transformation, cause troubles to our customers which they are not now having?

S. L. HOYT:[2] It happened that it was my job during the war to make observations on the deoxidation of steel, as made in the open-hearth furnace and also the electric furnace practice. That work took me around to many of the leading steel companies in this country, and naturally I took occasion to discuss this important phase of steel manufacture with everybody with whom I came in contact, from the melter on the furnace, the metallurgist, to the metallographist in the laboratory, etc. While I had an extremely interesting time, such discussions did not unravel the mysteries which surround the processes of steel manufacture, particularly the deoxidation of steel.

I think it would be interesting to speculate on the likelihood of uncovering the facts which Dr. Herty presented in this brief paper by any such means as were available during that study in 1918 and 1919. On the other hand, the work which Dr. Herty and his associates have done in Pittsburgh has led directly to this type of information, and it seems to me that this paper which he has presented will occupy a really notable position in the publications which have issued from that work. It is couched in terms which are understandable

[1]Metallurgist, Homestead Works, Carnegie Steel Company, Pittsburgh.
[2]Director of research, A. O. Smith Corporation, Milwaukee.

alike to the open-hearth melter, the steel manufacturer, the plant metallurgist, and in fact any who are interested in steel metallurgy. This paper gives them a means by which problems of this kind can be intelligently discussed, or which gives an intelligent conception of the problem. To me it is truly amazing that steels of simple compositions, but subject to slightly different variations during deoxidation, actually exhibit such fundamentally different characteristics. Certainly, the difference in impact value which Dr. Herty reports at sub-zero temperature for steels which are essentially of the same composition and which would be used for essentially the same purposes, is very remarkable.

In closing, I cannot fail to express my congratulations to Dr. Herty upon giving us this paper, brief though it is, and also to express the hope that in the future we may still continue to have the benefit of his experience and knowledge in this important field.

A. C. JONES:[3] Dr. Herty has very clearly presented to us data of great significance to the producer of steel who is trying to get the most out of his product. The information that he has shown accounts for some of the inconsistencies that have been experienced, but not understood or explained.

One such case from my own experience I shall present, which seems to be related to this effect: Pearlitic manganese steel of the following composition: Carbon 0.34 per cent, silicon 0.38 per cent, manganese 1.44 per cent, made in an electric furnace (acid practice) was treated with 5 ounces of aluminum per ton added to the large tea pot ladle at the furnace. Test blocks were then cast with shank pots as follows:

A.—No aluminum to shank pot.

B.—32 ounces of aluminum rod per ton.

C.—32 ounces of aluminum per ton as ferroaluminum (60 per cent aluminum).

The blocks were then heat treated, tensile and impact tests being made of specimens that had been given the treatment which follows:

1. Normalized—1650 degrees Fahr. (held at temperature 40 minutes).

2. Normalized—1650 degrees Fahr. (40 minutes) and drawn at 1225 degrees Fahr. for 1 hour.

The tensile and impact values obtained are shown as follows:

		Tensile Strength	Yield Point	Per Cent Elong. in 2"	Red. of Area	Charpy Impact (Ft. Lbs.)
Normalized only	A. (5 oz. Aluminum per ton to large ladle)	96,000	56,500	26.6	51.8	9.8
	B. (5 oz. Aluminum plus 32 oz. Aluminum per ton)	94,750	60,250	21.9	33.2	17.7
	C. (5 oz. Aluminum plus 32 oz. Aluminum per ton as Ferroaluminum)	95,500	60,500	22.7	37.9	19.6
Normalized and Drawn	A. (5 oz. Aluminum per ton to large ladle)	88,000	48,750	24.2	52.1	20.3
	B. (5 oz. Aluminum plus 32 oz. Aluminum per ton)	84,500	51,650	26.6	47.7	17.7
	C. (5 oz. Aluminum plus 32 oz. Aluminum per ton as Ferroaluminum)	83,500	51,500	26.6	51.0	21.0

The metal with a minimum of aluminum yielded satisfactory tensile values, but poor impact resistance, with a straight normalizing treatment, whereas with

[3]Research engineer, Lebanon Steel Foundry, Lebanon, Pa.

an excess of aluminum the impact values were about twice as great, even though the ductility was less. But with a draw treatment following the normalizing, the impact figures of A are raised to the level of B and C. This prompts me to ask Dr. Herty what heat treatment was given the specimens, test results of which are given in Table I.

Sims and Lillieqvist, in a paper presented at the February, 1932, meeting of the A.I.M.E. in New York, emphasized the point that to obtain good ductility (elongation and reduction of area) in steel treated with more than a modicum of aluminum, it was desirable to have a moderate iron oxide content so that the steel unetched would show a random distribution of round inclusions instead of the chain-like sonims caught in the grain boundaries, and which are typical of over-reduced steel in the electric furnace treated with an excess of aluminum (from ½ to 2 pounds per ton). They also developed the point that some of these nonmetallic inclusions are soluble to a degree that was not fully appreciated, and that holding the steel for 45 minutes in the ladle to allow the nonmetallics to rise to the surface did not yield steel that appeared markedly cleaner than metal from the same heat poured after a few minutes.

Therefore, it would seem that there must be a balance between the oxide in the bath and aluminum to be added with respect to getting the combination of maximum ductility with high impact resistance. This then leads to the thought as to what the result in Table I, Steel No. 4 might have been, had the metal been deoxidized with only aluminum and not with silicon, manganese and aluminum. I would like to have Dr. Herty's opinion on these points.

Author's Reply

C. H. Herty, Jr.: The paper to which Mr. Jones refers was given two or three years ago. I was not able to be present at the New York meeting at that time, and since then on five different occasions various people have tried to get Sims and myself at the same meeting, and it just happens (possibly luckily for me) that if I am there he is not, so we never have been able to battle the thing out. I get this decided impression from reading Sims' paper and discussion with our work thrown into it, that Sims believes that the inclusions are soluble, and we agree with him perfectly provided he specifies that they are largely sulphides, because I believe that sulphides are soluble in liquid state, and they come out of solution during the process of solidification.

It is inconceivable that a manganese silicate should be highly soluble in liquid steel, but when steel is deoxidized, the amount of sulphide and oxide in the steel is changed. If a heat is killed strongly with aluminum, the MnO content of the steel is low, and if it is killed with silicon the MnO content may be quite high, so there is a good opportunity of MnO fluxing with the sulphides as they come out of solution. With a heat with no MnO, the sulphides will come out by themselves with no fluxing and they will be found around the grain boundaries as very small particles. There is one thing we do not know and that is the effect of metallic aluminum in steel on the solubility of sulphides. For example, we know that if the manganese content of the steel is raised an entirely different type of inclusion results. A globular inclusion results if the manganese is up to 0.30 per cent. If it is 0.10 per cent manganese, a grain boundary inclusion of iron sulphide results. This is due to the change of solu-

bility with temperature which, as the steel solidifies, causes the manganese sulphide to precipitate early enough to have a chance to flux. The iron sulphide it so soluble it comes out very late, resulting in a chain around the crystal. Aluminum may have the same effect as manganese in changing the solubility of the sulphide. It may be that when there is an excess of aluminum with very little silica and MnO and no FeO there is nothing to flux the sulphide that comes out. As far as I can see, one cannot pick any flaws in the thought that it is a combination of the fluxing of sulphide inclusions with FeO, MnO or SiO_2 or the effect of metallic aluminum on the solubility. Either one would explain the situation in Sims' experiment where he put iron oxide into a ladle, half of which had been poured into a casting, and found that the half that had been poured without iron oxide but with aluminum was very short and that the other half had high ductility, indicates that either all metallic aluminum was eliminated by the iron oxide addition, or enough FeO, MnO and silica was formed after the elimination of aluminum, that there was a chance to flux the sulphide inclusions. If you look in Sims' paper and on the slides which he gave at the open-hearth meeting a year ago in June at Chicago (they are all published in the minutes of the open-hearth committee) you will see that the inclusions which cause low ductility gave every appearance of being sulphides and not oxides, because the globular inclusions were either typical silicates or typical manganese sulphides, dark and light, but the inclusions around the grain boundaries were entirely a light gray. So I think Sims' method of getting around low ductility is 100 per cent correct. I do not think his reasoning was right, but nevertheless he has the result.

The specimens on which impact values are given were normalized at 1650 degrees Fahr. (900 degrees Cent.).

Dr. Chipman's analysis of the steel SMA-15 has been of great help in our conception of the action of aluminum in deoxidation. The fact that this steel had such small traces of FeO no doubt contributed largely to its properties as set forth in Tables I and II.

Mr. Graham has brought up a very interesting point, in that some, at present, indefinite factor, in the raw materials may well exert an influence on the behavior of steel for a given method of deoxidation. A research program on this phase of steel-making would undoubtedly be of very great value to the producer of steel.

Dr. Hoyt's remarks are very deeply appreciated. The results which he has shown on the metallurgy of welding, in another paper at this meeting, seem to fit in beautifully with those given in this paper. This indicates that any process involving liquid steel, and possibly iron, must be treated with the same fundamentals, a point which is worth keeping in mind.

In answer to Mr. Kinear's question may I say that we have done no work with these extremely fine-grained steels in very large sections, but we certainly can see that if the grain-size is fine enough (which will be somewhere beyond No. 8 by a fine enough dispersion of alumina and a low enough content of oxide) a point would be reached where there are certain things that we do not anticipate now would happen. In other words, you could go too far in that direction just the same way that you did not go far enough if you used silicon by itself.

THE METASTABILITY OF CEMENTITE

By H. A. Schwartz

Abstract

One who engages in an experimental verification of metastability of cementite may be accused of "rediscovering the obvious." Since, however, this phenomenon has been seriously disputed on thermodynamic grounds by a metallurgist of repute, and since also data as to the CH_4-H equilibrium with Fe_3C have been published by highly skilled observers which are inconsistent with such metastability, a formal experimental treatment of the problem seems called for in order that an error, in either direction, may not be perpetuated.

It is shown below that in an iron-carbon alloy containing also 0.03 per cent silicon and not over 0.04 per cent of other elements, the reaction

$$Fe_3C = 3\ Fe + C$$

proceeds to the right at all temperatures from 630 degrees Cent. (1165 degrees Fahr.) to above the eutectic melting point.

The A_1 stable critical point is found 15 degrees Cent. (27 degrees Fahr.) above A_1 metastable in this alloy.

Introduction

THE earliest iron-carbon diagrams of Roberts-Austin and of Roozeboom included an area below the eutectic freezing point in which graphite was considered to be stable while below this area, which was perhaps 100 degrees Cent. (180 degrees Fahr.) or more wide, cementite was supposed to be the stable phase (1)*.

Very soon the opinion gained ground that the system Fe-C was always stable toward the system Fe-cementite in the solid state at least. The conditions are commonly represented by a "double" diagram in which the eutectic and eutectoid temperatures are higher in the Fe-C system than in the Fe-cementite system and the A_{gr} line is to the left of the A_{cm} line.

*The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Sixteenth Annual Convention of the Society held in New York City, October 1 to 5, 1934. The author H. A. Schwartz is a member of the society and is manager of research, National Malleable and Steel Casting Co., Cleveland. Manuscript received June 15, 1934.

Very lately Yap, Chu Phay (2) has put forward on thermodynamic grounds the thought that cementite is stable at temperatures considerably below the eutectic melting point but above say 700 degrees Cent. (1290 degrees Fahr.). His reasoning is based on a calculation of the free energy of the reaction

$$3\ Fe + C \rightleftarrows Fe_3C$$

at various temperatures, and is, in principle, apparently unassailable. The quantitative magnitude of this free energy and even possibly its algebraic sign will depend upon the data used in the calculation which includes the specific heats of iron (in the proper allotropic form), graphite and cementite; the heat of formation of cementite at some one temperature and the free energy of the reaction at some one known temperature. Unfortunately, the authorities do not agree upon certain of these constants within differences which may very greatly affect the result of the calculation and hence determine the temperature where, if at all, the calculated free energy changes sign. Yap chose what he believed to be the most reliable data but at one point this involved a decision between a heat of formation per gram molecule of Fe_3C of about —13,000 calories and one of about —4000 calories so that the correctness of his conclusions hinges in large part upon his skill in choosing, on not very clearly established grounds, between rather inconcordant data. One is even prone to wonder whether any of the data available to him are sufficiently beyond question to permit of unqualified acceptance of his or any other results. As a parallel problem consider that the best available data for the specific heat of α, γ and δ irons do not satisfactorily account for both the A_3 and A_4 points (3).

It appears worth while therefore, to consider whether there may not be more direct evidence as to the validity of his conclusions. It has been maintained (4) that in the liquid state iron-carbon alloys contain the latter element mainly as cementite. A temperature range in which cementite is stable in the solid should therefore have a lower boundary marked by a discontinuity in temperature change on cooling. Such a discontinuity has been observed by Carpenter and Keeling (5) for instance, but usually disregarded in later diagrams. Johansson and von Seth (6) have lately shown that the equilibria of the reactions

$$C + H_4 \leftrightarrows CH_4 \text{ and } Fe_3C + H_4 \rightleftarrows CH_4 + 3\ Fe$$

intersect at two temperatures, one by extrapolation near the eutectic

melting point and the other at about 900 degrees Cent. (1650 degrees Fahr.) in such a manner that cementite should be stable in this interval.

The greatest difference between the equilibrium gas mixtures for the two reactions in this range is about ⅕ per cent CH_4 in gases containing about 1 per cent of that gas. The temperatures of intersection are thus not very sensitive to the method of attack even though Yap's assumption is qualitatively confirmed. Schenck (7), on the other hand, reported no such crossing of gas equilibria although there is a faint indication of a possible reversal in sign of $\triangle F$ at about 950 degrees Cent. (1740 degrees Fahr.).

It would appear that the simplest check upon Yap's conclusion and hence upon the (net) accuracy of his data should be found in direct experiment to determine whether as a matter of observational fact, in approximately pure iron-carbon alloys graphite can, or can not, be converted into cementite or vice versa at chosen temperatures. The overwhelming experience of the malleable industry that graphitization goes on at temperatures far above those in which cementite is now said to be stable must be set aside for all these alloys contain very large amounts of silicon. The writer has elsewhere (8) touched upon the inconclusiveness of data obtained by extrapolation to zero silicon of data obtained in his own laboratory. Data obtained at very low silicon contents in the presence of significant amounts of other elements must also be rejected especially since the observations were made at temperatures sufficiently low so that a slight change in Yap's data might have put them outside his range of cementite stability.

We propose to gather facts which will determine *directly* whether or not the graphitizing reaction proceeds in the direction of combination of carbon at any such temperatures as h. .e been suggested and especially near 1000-1050 degrees Cent. (1830-1925 degrees Fahr.) where Johansson and von Seth's observations suggest that it is most likely to occur. Incidentally, we wish to gather such facts as we can regarding the iron-carbon system in general.

Experimental Methods

It was intended to use the purest iron-carbon alloy which could be made and completely graphitized. We have reported elsewhere (9) data tending to show that Armco and electrolytic iron melted in Acheson graphite in high vacuo do not graphitize well below A_1.

A new method of preparation was adopted which, although it did not improve on the purity of the alloy, was found to give graphitizable alloys. Armco iron was dissolved in HCl to remove sulphur and some phosphorus perhaps. Manganese was precipitated in HNO_3 solution with $KClO_3$. Iron (and Al) were precipitated with NH_4OH, the precipitate redissolved in HNO_3, evaporated and ignited to Fe_2O_3. This was partially reduced to Fe in H, possibly with removal of any residual sulphur and then fused in an Acheson graphite block in the Arsem furnace at a pressure of a few millimeters of mercury. We are indebted to Robert McLane for the carrying out of this preparation.

The form of the resulting 80-gram ingot can be judged from Fig. 1. It is significant as will be pointed out later. The ingot was sealed into a hard glass tube at a pressure of less than 1 micron through the kind co-operation of W. P. Sykes of the General Electric Company and was heated 2000 hours at about 650 degrees Cent. (1200 degrees Fahr.). The tube had collapsed tightly on the specimen. The analysis of the material was as follows:

Table 1
Analysis of Material Used in These Tests

C	5.07
Si	0.03
S	0.014
Mn	Trace
Al	<0.02
Cr	Trace
P	<0.005
Cu	None
Fe	94.8
Error and undetermined	0.061

The error may well reside in the iron and carbon determinations. There appears to be no reason to suspect the presence of detectable amounts of elements not looked for. Nearly all iron samples contain undeterminable traces of Ti and Mo which, though not specifically looked for, can hardly account for more than a very few thousandths of 1 per cent of the alloy.

Allowing for such traces and for the amount by which aluminum and phosphorus may be less than the possible maxima (the least quantitatively measurable amounts on the sample taken) it seems safe to say that the total impurities in the alloy lie between 0.05 and 0.07 per cent. By trace is meant an amount qualitatively detectable by color methods but undeterminable quantitatively. It may be roughly appraised at a few thousandths of 1 per cent.

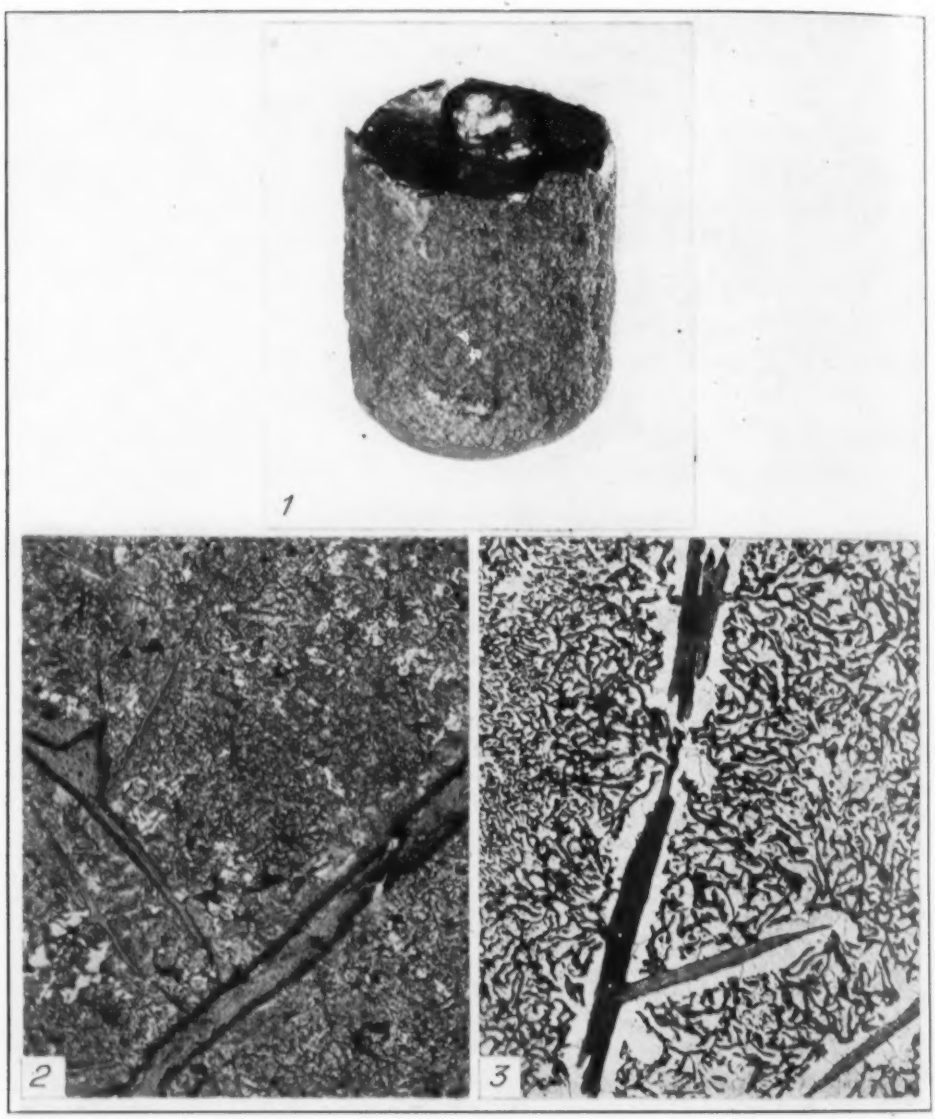

Fig. 1—Photograph of the 80-Gram Ingot Used in Making these Investigations. × 2.

Figs. 2 and 3—Photomicrographs of the Material Before and After Treatment. × 100.

The carbon content, not used in subsequent calculations, is subject to the errors of sampling occurring in so highly graphitic material. The iron determination includes the identical sampling error. Neither determination can be guaranteed as to the absolute accuracy but their sum is probably free from sampling errors.

Since the amount of material was limited, analyses could not be made on samples of desirable size. It is likely that the values are

conservatively high. Unfortunately, the purity of the material was not increased over what might have been obtained by simpler methods.

Photomicrographs of the material before and after heat treatment are shown in Figs. 2 and 3. It is evident that the specimen is graphitized to completion by the heat treatment chosen. The flaky character of the graphite should be noticed.

Critical point curves were run on Leeds and Northrup equipment to determine the relative displacement of the A_1 stable and metastable points. As has been frequently done in this and other laboratories, the displacement was evaluated from the change in the curves obtained on the first and second heatings. Fig. 4 reproduces the autographic record made by the apparatus in that region in which we are interested.

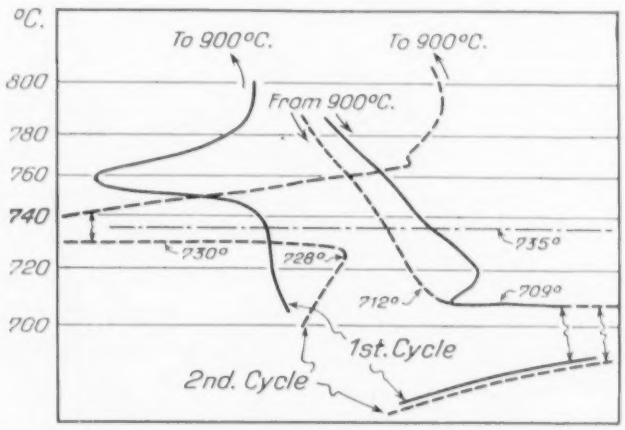

Fig. 4—Reproduction of Autographic Record Made by the Apparatus in that Region Which is Discussed.

The remainder of the experimentation consisted in a series of heat treatments of the parent material in order to determine the direction and completeness of the graphitizing reaction as a function of temperature in the range from somewhat below A_1 where there is agreement that pure cementite is metastable to as near the eutectic freezing point as we might approach.

Since there was occasion also to study these phenomena in the metal in an approximately graphite-free condition it was necessary to remelt and cool quickly a portion of the material.

Filings of the metal were introduced into a cup in the vertical carbon electrode of a projector arc lamp, quickly fused for perhaps one or two minutes and the resulting bead shaken into water with-

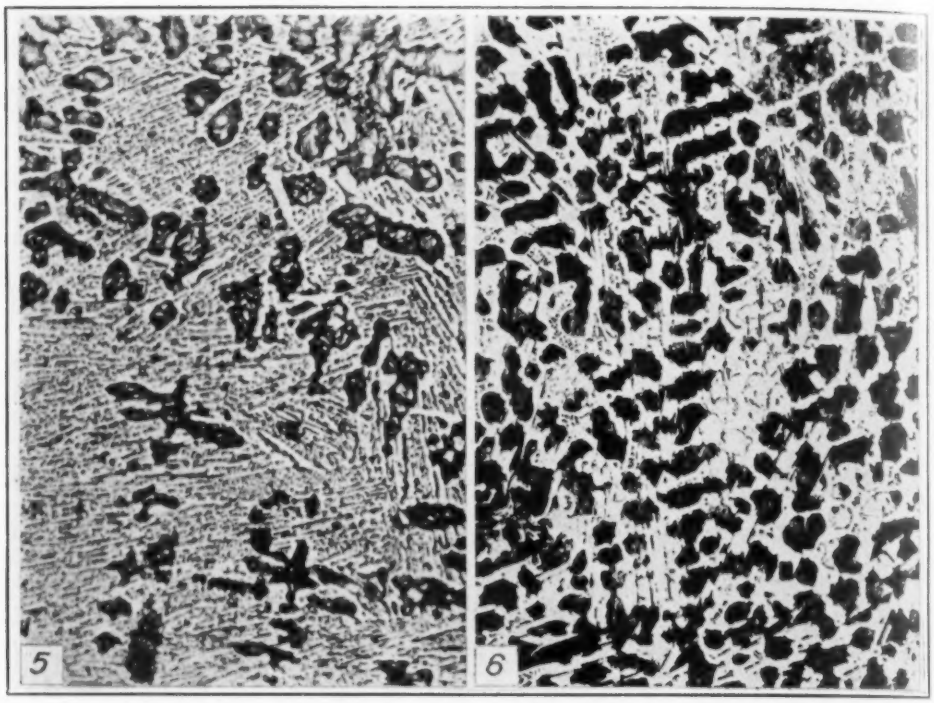

Fig. 5—Structure of Bead After Water-Quenching from the Melt. × 500.
Fig. 6—Structure of Bead Quickly Cooled with Electrode after Current was Interrupted. × 100.

out breaking the arc, when possible; Figs. 5 and 6 show the microstructure of the resulting beads two or three millimeters in diameter, the former water-quenched, the latter, which would not shake out, cooled quickly as the electrode cooled when the current was interrupted.

To avoid the contaminating effect of air and also to keep the product hypereutectic a further lot of filings was remelted in the apparatus shown in Fig. 7. The inner special crucible was machined from Acheson graphite.

Crucible and contents were water-quenched after the contents were molten and still covered with a thick layer of powdered graphite. Fig. 8 is a micrograph of the resulting slug. It consists of a matrix of very fine ledeburite with here and there large thin flakes of (proeutectic?) graphite. Some needles of proeutectic cementite were also encountered though none are shown in the photomicrograph.

Two methods of heat treatment suggest themselves. That due to Rosenhain in which the specimen is quenched in a stream of water sucked by vacuum through the hot furnace tube has the merit

of preserving as nearly unaltered as possible the condition at the moment of quenching. Our heat treatments are frequently quite long and the satisfactory exclusion of air presented difficulties. Filling the apparatus with (tank) nitrogen at a slight positive pressure was not always more satisfactory, involving decarburization by impurities in the gas or perhaps by water vapor, since for purposes of control the gas was stored over water. This decarburization became of considerable interest when attempting to correlate our data with

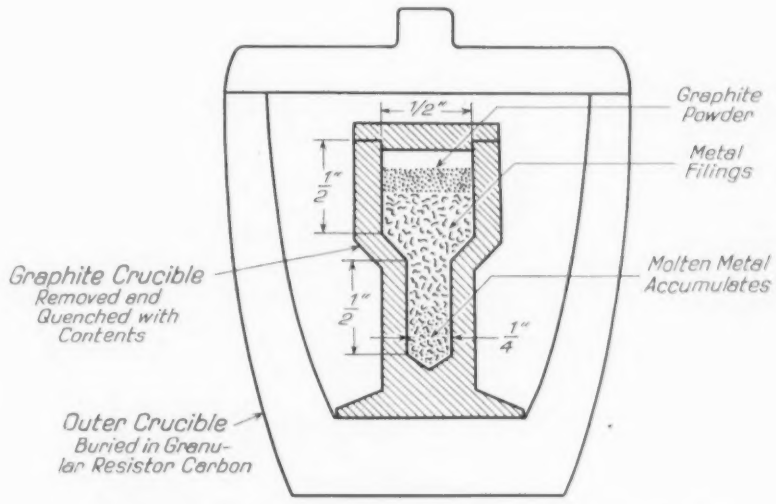

Fig. 7—Sketch Showing Method of Melting Filings to Keep them Free from Air Contamination.

others in the course of the A_{cm} line, a subject to which a separate section will be given.

Specimens sealed in quartz tubes of 2 to 4-millimeter bore at a pressure of about 1 millimeter of mercury can be heat treated for any reasonable time without significant decarburization. They can be cooled fairly rapidly by quenching or even in air on removing from the furnace. To attain this result, however, the specimens must be very small which makes impossible any analytical work by the usual methods. Where the mere direction of action is to be determined this is of little consequence for metallographic methods often suffice.

These limitations prevented our adding any data of importance to previous investigations as to the locus of the A_{gr} line. For the purpose of qualitatively testing the Yap thesis it was always possible to choose one or the other method of heat treatment and obtain the desired observational facts.

Experimental Data

We assemble here all of the observational data on heat treated samples. The significance of the apparent diversity of treatments, data and methods will appear more clearly in the subsequent discussion of the data in a separate section. The numbering is practically in chronological sequence.

Experiment 1.

Specimens of the completely graphitized material were sealed into quartz tubes under diminished pressure and heated at a temperature between 1025 and 1050 degrees Cent. (1875-1925 degrees Fahr.) for about two hours and about 200 hours. This temperature is so high that specimens of slender form held the longer time tend to become ellipsoid in shape under surface tension.

The depth of color obtained on dissolving these materials in HNO_3 as in the usual color method for combined carbon was compared with the following results.

Table II
Color Intensity When Dissolved in Nitric Acid

Time at 1025-1050 Degrees Cent.	Relative Intensity of Color
1.95 hours	1 (taken as standard)
196 hours	0.85

We do not regard these results as absolute measures of combined carbon. Figs. 9 and 10 are photomicrographs of these specimens. The white constituent is identified as cementite (proeutectoid?).

The relative amounts of cementite and martensitic matrix were determined by the intercept planimeter at magnifications such that a comparably coarse structure was given for each specimen with the following results.

Table III
Relative Amounts of Cementite and Martensite

Time Heated	Per Cent Cementite
1.95 hours	25.34
196 hours	21.97

We cannot be certain of the carbon content of either the cementite (10) or martensite hence not of the total metallic phase but

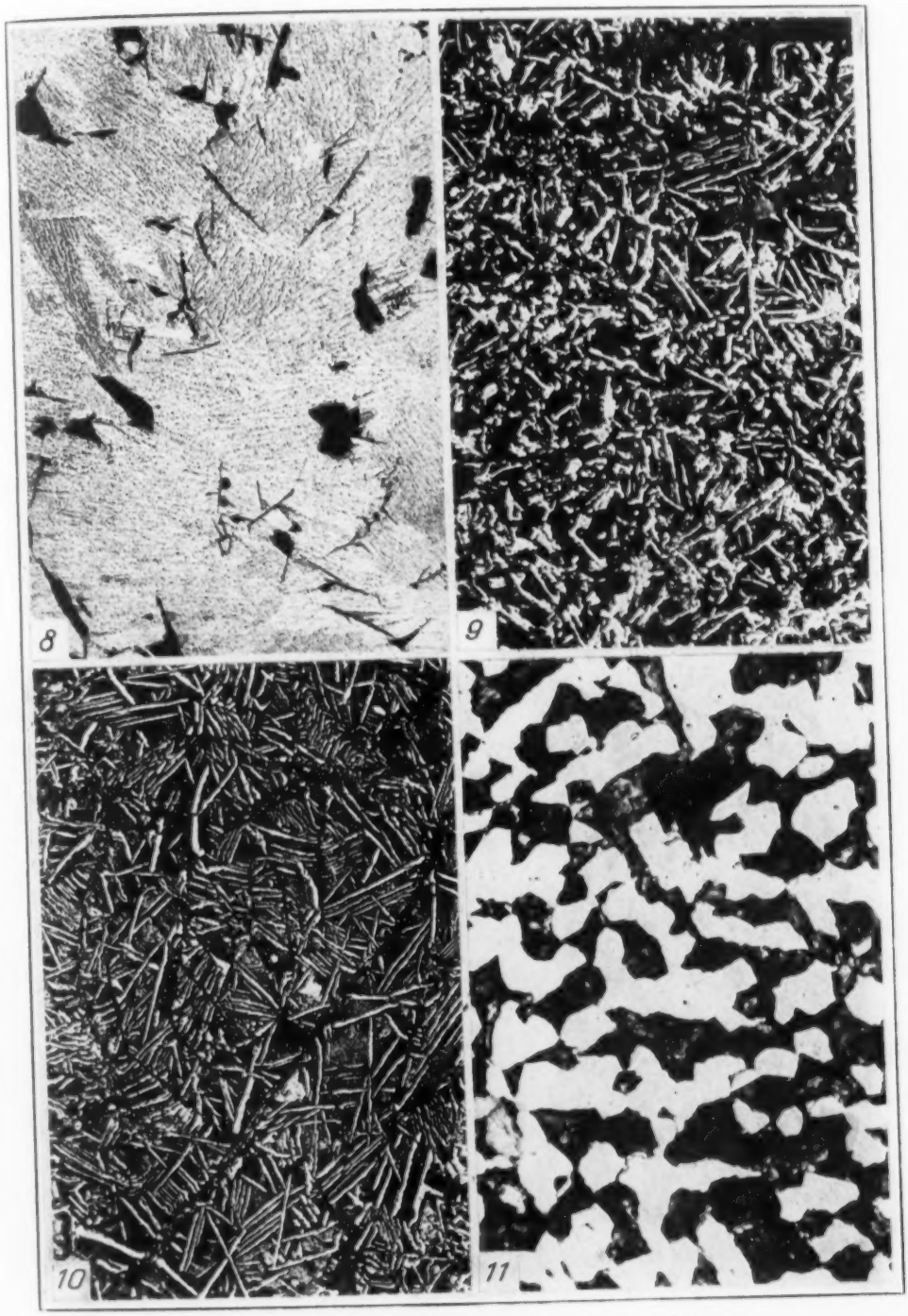

Fig. 8—Photomicrograph of Slug Melted as in Fig. 7. × 100.
Figs. 9 and 10—Photomicrographs of Specimens Treated as in Experiment 1. Fig. 9 × 200. Fig. 10 × 100.
Fig. 11—Photomicrograph of Specimen Treated as in Experiment 3. × 500.

it would seem likely that they should be at least similar in the two preparations.

Experiment 2.

Specimens of the material were sealed into quartz tubes at low pressure. One tube was introduced into a furnace at 823 degrees Cent. (1515 degrees Fahr.) (in terms of the same couple used for drawing the critical point curves), the temperature was lowered to the range 732-739 degrees Cent. (1350-1360 degrees Fahr.) and the second specimen introduced and the temperature range maintained for one and one-half hours when both tubes were withdrawn and air-cooled on an iron plate. Neither specimen showed any pearlite. Either this temperature is below both Ar_1 and Ac_1 stable or the graphitizing reaction just below A_1 is extremely rapid.

Experiment 3.

Half of each of the two beads resulting from the remelting of the material in the open arc were sealed into an evacuated quartz tube introduced into a furnace at 1015 degrees Cent. (1860 degrees Fahr.) reaching the furnace temperature in about three minutes. The temperature was maintained near 1000 degrees Cent. (1830 degrees Fahr.) for one hour and the tube and specimens raked out and quenched in water. Perhaps one minute may have been occupied in quenching. The specimens had remained perfectly bright. Photomicrographs are shown in Figs. 11 and 12. The former is the specimen quenched in water from the arc and is comparable with Fig. 5.

Experiment 4.

A second portion of the water-quenched specimen, sealed in an evacuated quartz tube, was heated at about 715 degrees Cent. (1320 degrees Fahr.) for 99½ hours, quenched and examined metallographically. A micrograph is shown in Fig. 13.

Experiment 5.

A portion of the crucible remelted material sealed into quartz was heated near to but just above A_1 for 232½ hours. The resulting microstructure is shown in Fig. 14.

Experiment 6.

Another specimen of the same fusion was heated in vacuo,

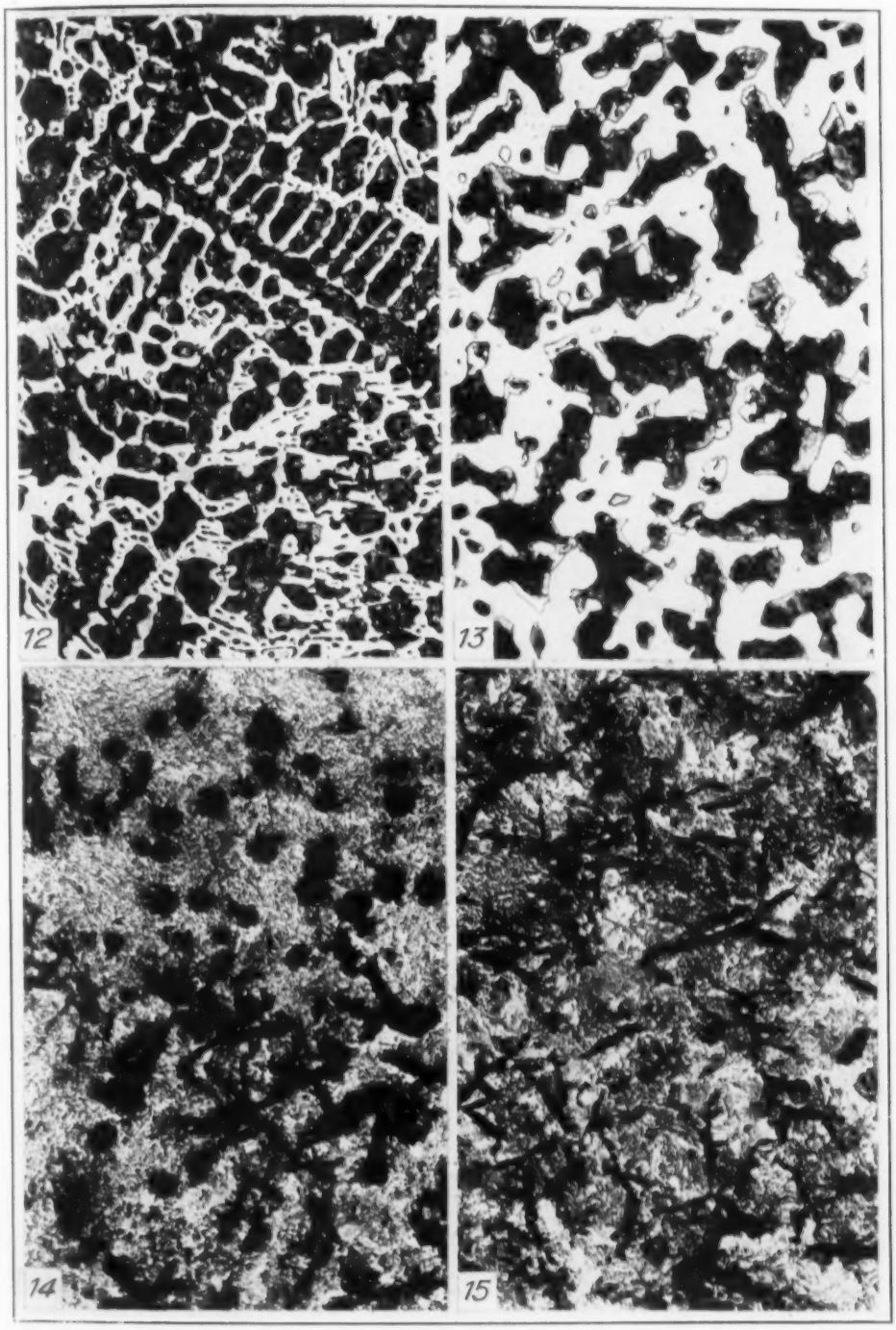

Fig. 12—Photomicrograph of Specimen Treated as in Experiment 3. × 100.
Fig. 13—Photomicrograph of Specimen Treated as in Experiment 4. × 500.
Fig. 14—Photomicrograph of Specimen Treated as in Experiment 5. × 100.
Fig. 15—Photomicrograph of Specimen Treated as in Experiment 6. × 100.

sealed into quartz for 50 hours at approximately 1090 degrees Cent. (1995 degrees Fahr.). Unfortunately, owing to failure of the furnace winding it cooled to below the critical in perhaps one hour instead of a fraction of a minute as by quenching. Its structure is shown in Fig. 15 showing the entire disappearance of cementite.

Experiment 7.

A specimen of the original metal heated for two hours at 1060 degrees Cent. (1940 degrees Fahr.) in the Rosenhain apparatus and quenched contained about 1.32 per cent combined carbon and an excess of graphite.

Experiment 8.

Specimens of the original metal heated over night at 795 degrees Cent. (1465 degrees Fahr.) and two hours at 875 degrees Cent. (1605 degrees Fahr.) showed no hardening on quenching although the latter showed under the microscope a few martensitic spots.

Experiment 9.

A specimen of the original metal heated by the Rosenhain method for 4¾ hours at 940 degrees Cent. (1725 degrees Fahr.) contained 0.08 per cent combined carbon in the presence of excess graphite.

Experiment 10.

A specimen of the re-fused material sealed into a quartz tube at diminished pressure and held for two hours at a temperature of 1120 degrees Cent. (2050 degrees Fahr.) and cooled had the structure shown in Fig. 16 which shows clearly the further precipitation of graphite.

Experiment 11.

A specimen of the material remelted in the crucible and sealed into a quartz tube at diminished pressure was raised to a temperature of about 1050 to 1100 degrees Cent. (1920-2010 degrees Fahr.) for a few hours, cooled in 24 hours to about 830 degrees Cent. (1525 degrees Fahr.) in which range it was held for about 50 hours and removed. Its microstructure is shown in Fig. 17, the matrix being approximately pearlitic in which massive carbide and graphite are embedded.

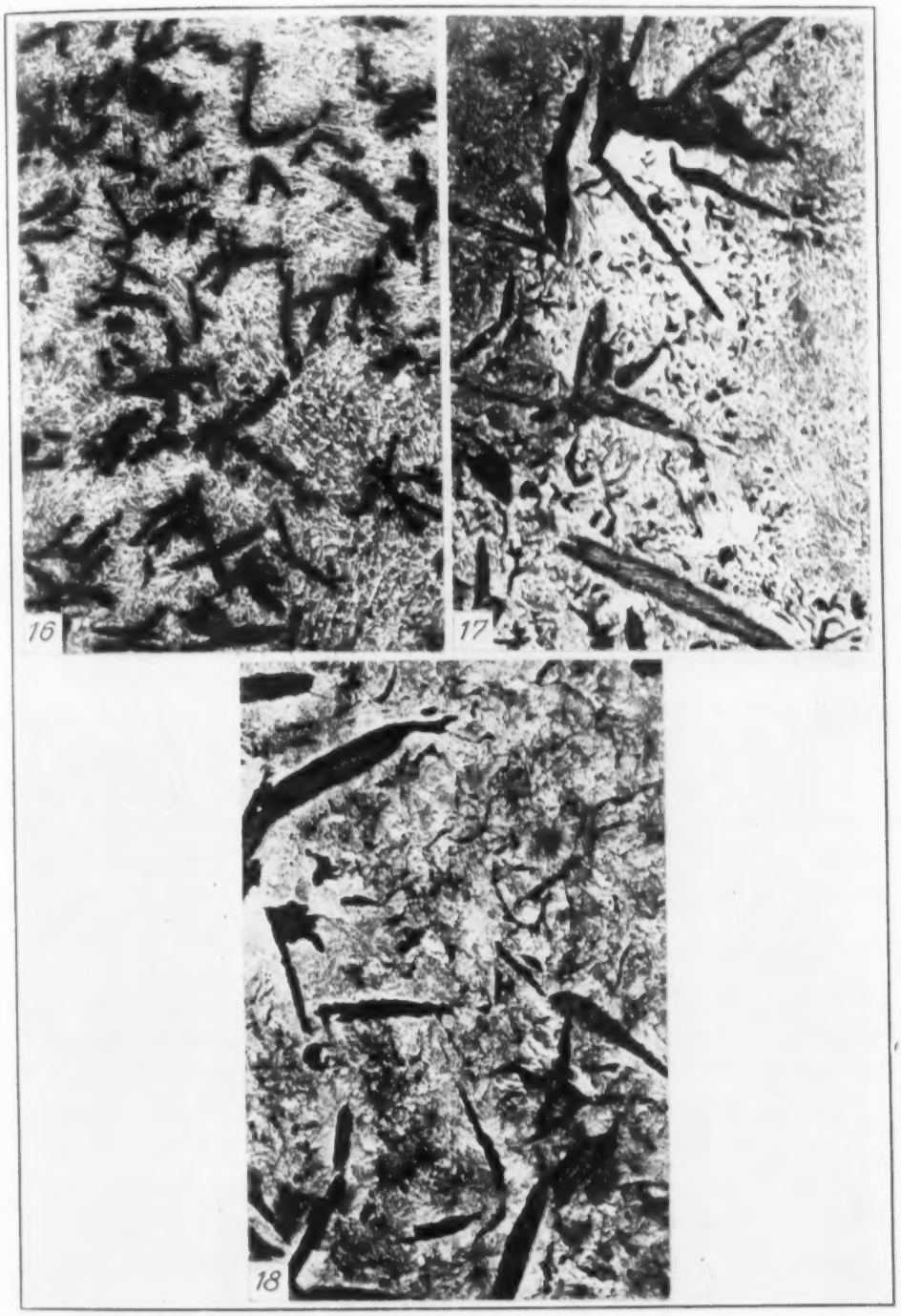

Fig. 16—Photomicrograph of Specimen Treated as in Experiment 10. × 100.
Fig. 17—Photomicrograph of Specimen Treated as in Experiment 11. × 100.
Fig. 18—Photomicrograph of Specimen Treated as in Experiment 12. ×100.

Experiment 12.

A specimen of the original graphitic material was sealed into a tube at diminished pressure and held near 830 degrees Cent. (1525 degrees Fahr.) for about 650 hours showing after removing in the usual manner involving cooling in a minute or so, the pearlitic-sorbitic structure of Fig. 18. The specimen contained 0.81 per cent combined carbon, by color, being too small for analysis by combustion for total carbon and graphite.

Discussion of Experimental Data

Admittedly the alloy is not as pure as could be wished. It seems likely that the significant amount of silicon and the possibly very small amount of aluminum, for which we know only an upper limit, as well as the small sulphur content, have been picked up during the melting operation. It is generally recognized that in preparing very pure iron, fusion is to be avoided, a precaution which cannot here be considered in view of the need of securing an alloy whose composition is consistent with the presence of considerable eutectic cementite should that phase prove stable.

We can scarcely say whether an alloy approaching purity no more closely than does ours offers a satisfactory approach to a pure binary system for the present purpose; i.e., whether its cementite is neither more nor less stable than that of an absolutely pure binary alloy. We can, however, form some opinion as to whether its thermal properties are likely to differ in an observable degree from those of pure iron.

Calculations such as Yap's involve consideration of specific heats and of heats of combustion. Since specific heat is an atomic function, it seems most unlikely that the specific heat of silicon dissolved in iron can differ greatly from its specific heat dissolved in cementite. If it is dissolved in iron even in the presence of cementite then its specific heat is obviously not at all altered by graphitization. Therefore the differences in specific heat between Fe_3C and a mechanical mixture of its components would be altered very little by the presence of silicon in solution once in cementite and then in iron. This coupled with the small concentration of silicon would seem sufficient reason for assuming that the slight impurity present (mutatis mutandis for the elements other than silicon) would not alter ΔC_p for the graphitizing change by an amount detectable by

even very good calorimetric work. Further, the present alloy is incomparably purer than the material used by Umino (11) in his fundamental researches on the specific heats upon which we must depend for ΔC_p.

The heat of formation of Fe_3C is derived for the present purpose by considering the difference between the heat of combustion of Fe_3C and of its components.

If the silicon (or other impurity) be present in the same molecular state before and after graphitization it will obviously not affect the heat of formation, ΔH, of cementite. If it were originally a constituent of cementite, (in solution or combination), then its release from cementite may involve the evolution or absorption of heat. The heat of solution of metals in other metals is probably not greatly different in different solvents, being at least similar in magnitude to the latent heat of fusion, a fact pointed out for Fe_3C by Yap (2).

The heat of combustion of silicon dissolved in iron and in cementite should therefore be very similar. If the silicon be present as the *same* compound (in solution) in iron and the carbide instead of as the atom, the same reasoning holds.

The heat of combustion of silicon to SiO_2 is given in round numbers as 191,000 calories per gram atom or approximately 7000 calories per gram. One gram molecule of cementite contains 168 grams of iron which would in our alloy be accompanied by $0.0003 \times 168 = .05$ grams of silicon whose heat of combustion would be 350 calories. Making no allowance for a possible diminution of this value by the heat of formation of silicides, which if present are almost certainly exothermic and would thus reduce the correction, the heat of combustion of one gram molecule of cementite having our silicon content would be 350 calories greater than that of the pure substance. This is about 2½ per cent of the heat of formation determined by Brodie, Jennings and Hayes (12) and accepted by Yap. These workers in three reported determinations obtained -76.7, -79.3 and -70.7 for the constant in question. They thus got values differing by 5 per cent or more from their own mean.

Furthermore, since they also started with Armco iron and fused in the presence of graphite, their chance of contamination was about the same as ours and their data should, therefore, apply in the present case with no perceptible error. Unfortunately, they did not report actual analyses of their cementite for other elements than iron and

carbon. These two totaled exactly 100 per cent but they themselves rightly pointed out that this agreement did not preclude the presence of some few hundredths of 1 per cent of impurities. To attempt any prediction as to the effect of the existing impurities on the free energy of formation of cementite would be to prejudge the issue.

The shape of the ingot, shown in Fig. 1, shows very clearly that an expansion took place between the time of solidification of the outer shell and the interior.

The extrusion of a drop, here observed, does not occur with pure iron or steels or with white cast irons. It seems reasonable to suppose, therefore, that it represents the increase of volume due to graphitization. The graphitization of a solid shell cannot exert pressure upon the liquid interior for the increase in circumference due to expansion would more than counterbalance the increase in thickness (unless the thickness equals the outer radius when no liquid remains).

It is commonly accepted that liquid cast irons contain their carbon preponderantly as cementite. If then cementite is to be stable in the liquid phase but hypereutectic alloys graphitize during freezing, it seems not unlikely that the *solid* cementite of the alloy is doing the graphitizing, i.e., that solid cementite is metastable above about the eutectic temperature.

The micrograph of the as-cast alloy, Fig. 2, suggests strongly that its graphite flakes grew in a material which was either liquid or at any rate so plastic as to indicate a temperature but little below the eutectic freezing point. This is not to say whether or not this metastability is continuously maintained to the temperature of about 650 degrees Cent. (1200 degrees Fahr.) at which this alloy was completely graphitized as shown in Fig. 3.

The existence of combined carbon in the as-cast specimens is not to be interpreted as proof of the existence of a zone of stability for cementite as Yap (12) concludes from Sanford's magnetic detection of pearlite in reheated and cooled malleable. The separation of pearlite during moderately slow cooling of malleable from above A_1 is so well known as not to require further proof. If a stable solid solution saturated with carbon in any form is cooled too rapidly to maintain equilibrium, especially in passing through A_1, the excess carbon may well crystallize as pearlitic cementite even if that be not the stable phase and if the cementite was formed only at the moment of crystallization.

It is a general rule (called by Tammann, Stufenregel) that, if several phases are possible differing in stability, a super-cooled solution deposits first the least stable. Thus the presence of pearlite in our alloy or in malleable when super-cooled would seem an evidence of metastability of cementite rather than of stability.

The metal remelted under the protection of graphite such as that in which it was originally melted in vacuo will graphitize quite slowly near A_1. This temperature is probably low enough to be in the temperature range in which cementite should be metastable according to Yap and is certainly so as compared with the Johannsen and von Seth observations. The temperature is, perhaps, 75 or 100 degrees Cent. (135-180 degrees Fahr.) above that at which the complete graphitization of the original ingot was accomplished.

The specimens remelted in the arc represented by Figs. 5 and 6 seem on microscopic evidence to be hypoeutectic, not hypereutectic, like the original alloy. The explanation lies in the probable loss of graphite while preparing the filings. On such minute specimens it is, of course, impossible to demonstrate that no changes of composition have been caused during the melting operation. Some oxidation is not impossible even though the "hearth" of the miniature furnace was completely enveloped by the carbon vapor of the arc.

This hypoeutectic alloy seems incapable of graphitization (experiments 3 and 4), and is, therefore, rejected for further use as not being comparable with the original graphitic material or the remelt under graphite.

The major part of this investigation represents efforts to observe the *direction* of the graphitizing reaction at various temperatures. It is accordingly not essential to know the temperatures with extreme precision especially because in long treatments some temperature variation is unavoidable. The temperatures were measured with a platinum, platinum-rhodium thermocouple whose error on direct comparison with standard couples was about 1 per cent. Readings were taken, however, not with a potentiometer but with an instrument of the milliammeter type whose temperature scale did not correspond to the thermocouple. The couple and indicator were accordingly calibrated together by comparison with two thermocouples of known e.m.f. read by an L and N Type K potentiometer. The working thermocouple had its cold junction maintained at 0 degree Cent. by immersion in mercury wells in a thermos bottle filled with melting ice. Readings could be taken to the nearest 5

degrees Cent. and the calibration was carried out with a precision greater than this but it is not improbable that some temperatures may be in error as much as 10 degrees Cent. In general, a precision of ± 10 degrees Cent. is to be understood as applying to all temperature readings except as applying to the A_1 point's location.

We interpret the recorded experiments as follows: The heat treatment involved in the original preparation demonstrates that at 630 degrees Cent. (1165 degrees Fahr.) the graphitizing reaction proceeds in the direction of graphite formation.

Experiment 1 is considered to demonstrate that at 1025 to 1050 degrees Cent. (1875-1925 degrees Fahr.) graphite dissolves in gamma iron but saturation is reached in about two hours and subsequent exposure does not produce massive cementite as it should if Fe_3C were stable at this temperature. The apparent decrease in agraphitic carbon with continuing treatment is not considered significant. It is assumed that it is not real but that the color carbon and metallography are both affected by differences in the completeness of rejection of proeutectoid cementite with slight differences in cooling rates.

Experiment 5 demonstrates that at a temperature just above the critical point, as shown metallographically, cementite will dissociate.

Experiment 6 demonstrates this dissociation at 1090 degrees Cent. (1995 degrees Fahr.), though not unequivocally. It might be asserted that all the graphitization occurred during cooling. There is no other evidence of such rapid graphitization at similar temperatures and the assumption may be safely discarded.

Experiment 7 is a quantitative elaboration of Experiment 1 to be touched upon in the next section.

Experiments 8 and 9, in which the presence of the moist N atmosphere may play an important part, demonstrate the slight or slow solubility of carbon in iron in the gamma range.

Experiment 10 demonstrates the dissociation of graphite at 1120 degrees Cent. (2050 degrees Fahr.).

Experiment 11 demonstrates that graphitization has progressed at high temperature or at 830 degrees Cent. (1525 degrees Fahr.) to a considerable degree but certainly not rapidly at the latter temperature.

Experiment 12 demonstrates the fact that massive cementite

does not re-form at 830 degrees Cent. (1525 degrees Fahr.) in a very long time.

We seem thus to have observed cementite to dissociate at the following temperatures:

Above the eutectic melting point, at 1120, 1090 degrees Cent. (2050-1995 degrees Fahr.), just above the critical point, and at 630 degrees Cent. (1165 degrees Fahr.).

We have failed to observe the formation of cementite from graphite and iron except in such forms as would occur during the cooling of supersaturated solution coming under the "Stufenregel" at the following temperatures:

Between 1025 and 1050 degrees Cent. (1875-1920 degrees Fahr.) and at 830 and 630 degrees Cent. (1525-1165 degrees Fahr.).

Such negative evidence is, of course, inconclusive; logically it furnishes support for the positive evidence only as indicating that the latter has not been contradicted.

The Solubility of Graphite in Gamma Iron

It is not claimed that our data, except as to the location of the A_1 (stable) point, are sufficiently precise or voluminous to attempt any revision of the stable iron-carbon diagram. Certain of our observations, however, throw some light upon the observations of others.

Consider first the location of the A_1 point. In Fig. 4 we find during the first heating, the first change of direction to be not very strongly marked but located somewhere between 730 and 735 degrees Cent. (1345-1355 degrees Fahr.), which should be taken as A_{e1} (stable). In the descending branch of the curve there is a slight inflection just above 735 degrees Cent (1355 degrees Fahr.) before we come to the sharp break at 709 degrees Cent. (1310 degrees Fahr.) marking Ar_1 (stable). On the second heating and cooling we find Ac_1 (metastable) quite sharply defined at 728 degrees Cent. (1340 degrees Fahr.) and Ar_1 (metastable) at 712 degrees Cent. (1315 degrees Fahr.). The absence of combined carbon in specimens heated near 735 degrees Cent. (1355 degrees Fahr.) no matter in which direction equilibrium is approached, confirms the conclusion that this temperature is below both Ac_1 stable and Ar_1 stable.

Comparing the first and second heating curves, Ac_1 (stable)

is somewhat over 7 degrees Cent. higher than Ac_1 (metastable) and Ar_1 (stable) 23 degrees Cent. higher than Ar_1 (metastable) judging by the first visible break in the curves or 30 and 26 degrees Cent. (54-47 degrees Fahr.) judging from the peaks of the curves. Assuming an equal lag for ascending and descending temperatures, A_1 (stable) is at 735 degrees Cent. (1355 degrees Fahr.) judging from the first break in the curves and at 740 degrees Cent. (1365 degrees Fahr.) judging by the peaks. Similarly, A_1 metastable is at 720 degrees Cent. (1328 degrees Fahr.) or 719½ degrees Cent. (1327 degrees Fahr.).

Our observations on A_1 metastable are thus close to the accepted value 721 degrees Cent. (1330 degrees Fahr.). The difference between A_1 (stable) and (metastable) depends largely upon the interpretation of our chart but having in mind the corroboration of the direct heat treating experiment we prefer to take for A_1 stable a temperature not under 735 degrees Cent. (1355 degrees Fahr.) which would give a difference between the two temperatures of about 15 degrees Cent. Körber and Oelsen (loc. cit.) accept 733 degrees Cent. (1355 degrees Fahr.). It seems likely that the graphite is so slowly soluble (or precipitable) in γ iron solution that the transformation is spread over a much longer range than that of the metastable system making the peaks of a differential temperature curve quite unreliable guides to the location of the transformation points. Indeed there is some question as to the interpretation of Experiment 2 which might perhaps mean that the solution even at 830 degrees Cent. (1525 degrees Fahr.) takes place so slowly that lack of combination of carbon is due to lack of time. Having in mind the speed at which solution takes place when determining critical points and that the specimens were protected from oxidation, this doubt can probably be dismissed from our minds with safety.

The temperature measurement in Experiment 2 was made with special precaution, comparing the thermocouple and potentiometer used with those used in the critical point determination. The temperatures are safely comparable to 1 degree Cent. and the value of A_1 stable found as part of this critical point determination furnishes the best possible calibration of the critical point apparatus showing it to be within 1 degree Cent. of correct.

The most acceptable determination of the A_{gr} line so far is probably that of Ruer and Ilgin (14). Becker (15) attacked the

problem by carburizing iron (in his case of variable silicon content) to saturation in contact with carbon. He obtained a series of results in very low carbon metal in which the lower end of A_{cr} did not pass below 900 degrees Cent. (1650 degrees Fahr.). In Fig. 19 have been plotted as thin lines the metastable iron-carbon

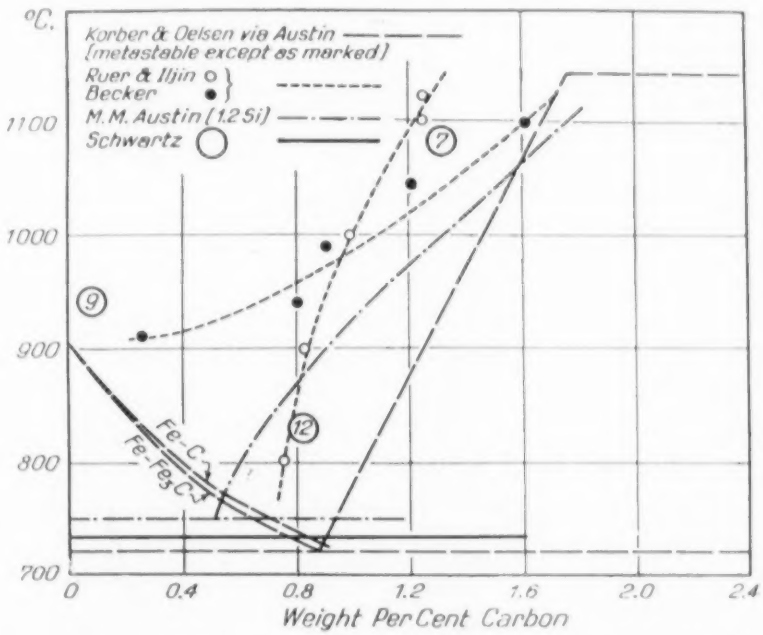

Fig. 19—Metastable Iron-Carbon Diagram as Accepted by Körber and Oelsen.

diagram as accepted by Körber and Oelsen (16) after a critical comparison of all the reliable observations with thermodynamic data.

Körber and Oelsen (15) have calculated the A_3 line from the heat of transformation of iron. Assuming Fe_3C to be the solute, the carbon concentration at 721 degrees Cent. (1330 degrees Fahr.) should be 0.84 per cent. Assuming graphite as the solute the carbon concentration at 735 degrees Cent. (1355 degrees Fahr.) should be 0.82 per cent.

It may be well to point out in passing that any attempt to use a single A_3 line for both the stable and metastable systems is permissible only if the solute in the two systems is identical. If we are to consider the possibility that the solute may be Fe_3C in one case and C in another, then the molar concentrations for a given weight concentration of carbon differ and two A_3 lines must exist. The numerical relations are such that if carbon and cementite mole-

cules each contain the same number of carbon atoms the postulate that the solute is carbon must give a higher value of A_3 which is presumably an indication that this system is the more stable. The stable A_3 line of Körber and Oelsen is also shown as a thin line in the Fig. In the Fig. have been inserted also the results of Ruer and Ilgin and of Becker for A_{gr} and the results of the late M. M. Austin of this laboratory for metal containing 1.2 per cent silicon. Dotted lines have been drawn by the present writer through the array of dots representing respectively Becker's and Ruer's determinations. Superimposed on all this is shown as a heavy line our determination of A_1 stable and three determinations of carbon solubility shown as large circles to indicate the limitation of precision from which these data suffer. These circles are numbered to show the experiment described in the preceding section to which they refer.

The observation of Experiment 7 is in a region where Becker and Ruer and Ilgin's results do not differ greatly and check either about equally well. Experiment 9 checks Becker and Experiment 12 checks Ruer and Ilgin. The significant difference in experiments 9 and 12 is that in the former there was exposure for a considerable time to moist nitrogen, in the latter contact with gas was almost completely prevented. The specimen of Experiment 9 showed some evidence of oxidation (by leakage or water vapor) and since Becker also was confronted with difficulties in suppressing oxidation it is suggested that the equilibrium which he reached involved oxygen in some form also.

It is to be noted that Ruer and Ilgin's data if extrapolated would intersect our A_1 stable line considerably to the left of the intersection of the theoretical A_3 (stable) line with our A_1. The intersection falls closely upon the theoretical A_3 metastable line.

One is not prepared to discuss this discrepancy on the basis of so limited an experimental background. If it be not due to observational error it may be necessary to seek an explanation by considering whether the carbon and cementite molecules contain but a single carbon atom.

Summary and Conclusion

A hypereutectic iron-carbon alloy was prepared containing 0.03 per cent silicon and probably not over 0.04 per cent of all other elements. Direct observations were made of the direction of the reaction

$$Fe_3C \leftrightarrows 3\ Fe + C$$

at a series of temperatures from 630 degrees Cent. (1165 degrees Fahr.) to above the eutectic melting point. Attempts were made to cause the reaction to proceed in both directions. Particular attention was given to the temperature interval between 1000 degrees Cent. (1830 degrees Fahr.) and the melting point.

The decomposition of cementite was observed at all temperatures, its formation (as distinguished from the crystallization of proeutectoid cementite from super-cooled solutions) never.

The stable A_1 point was located 15 degrees Cent. above the metastable A_1 which is in fair agreement with the accepted spread of about 13 degrees Cent.

Ruer and Ilgin's A_{gr} line was qualitatively confirmed and a possible cause of the discrepancy between their determinations and Becker's pointed out. Attention is called to the fact that the Ruer and Ilgin A_{gr} line does not intersect the stable A_1 line on the A_3 stable line computed from the heat of transformation of iron on the assumption of monatomic iron and carbon and ideality of solution.

It is concluded that direct experiment contradicts the thermodynamic deduction of Yap, Chu-Phay that cementite is metastable at temperatures lying above some undetermined value somewhat in excess of A_1. The same experiments are incompatible with the CH_4-H equilibrium observed by Johannsen and von Seth at temperatures somewhat below the eutectic melting point.

It is further concluded that some one or more of the thermodynamic data accepted by Yap must be in error and that more accurate knowledge of the fundamental free energies and heats of formation must be secured.

It is worthy of note that had Yap used the heat of formation of cementite determined by Watase who himself pointed to an experimental error in the determinations of Ruff and Gersten, the apparent stability of cementite would have been limited to a region near 900 degrees Cent. (1650 degrees Fahr.) which is, perhaps, not well suited for calculation as involving the A_3 perturbation.

Addendum

Since the preceding article was prepared the work of Pingault, Ann. Chim., Vol. XX, 1933, p. 371, has come to the writer's attention, Chemical Abstracts, Vol. XXVIII, 1934, p. 3040.

That observer produced cementite by treating iron (Carbon 0.03 per cent, silicon 0.005 per cent, manganese, trace, sulphur 0.002 per cent, phosphorus 0.009 per cent) as a 30 to 200 mesh powder in 50-gram lots with NaCN in the presence of air, which is indispensable. The time required was 30 hours at 800 degrees Cent. (1470 degrees Fahr.), 48 hours at 650 degrees Cent. (1200 degrees Fahr.), or 80 hours at 600 degrees Cent. (1110 degrees Fahr.). Pingault found that Fe_3C was thermodynamically unstable at ordinary temperature. Heated one hour at 1225 degrees Cent. (2235 degrees Fahr.) globules resembling high carbon cast iron and a powder rich in graphite resulted. It decomposed rapidly near the melting point of cast iron and after slow heating to 1000 degrees Cent. (1830 degrees Fahr.) showed what should be an A_1 point on cooling which seems evidence that iron was formed by decomposition.

The CO-CO_2 equilibrium with C and Fe_3C was studied and the curves found to intersect at 820 degrees Cent. (1510 degrees Fahr.). The latter observation would seem to contradict the metastability of cementite at both low and high temperatures (the abstract does not state in which direction the curves crossed).

The formation of Fe_3C at 600 to 800 degrees Cent. (1110-1470 degrees Fahr.) might be interpreted as evidence of its low temperature metastability or of the "Stufenregel" carbon entering the iron from the cyanide by first forming Fe_3C which has not dissociated in the time given.

The significance of a possible content of nitrogen seems not to have been closely considered.

Acknowledgment

The photomicrographs and critical point determinations are the work of C. H. Junge in the author's laboratory.

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DISCUSSION

Written Discussion: By M. L. Becker, National Physical Laboratory, Teddington, England.

I am glad to have the opportunity to discuss this paper by Dr. Schwartz. Most investigators now agree that pure iron carbide is metastable with respect to graphite at temperatures up to, and probably above, that of the austenite-cementite eutectic. There are, however, those who believe the reverse to be true over a certain range of temperature and we are indebted to Dr. Schwartz for reviewing the subject and bringing forward new and valuable experimental facts to clarify the issue.

Dr. Schwartz has referred to work carried out by the present writer[1] to determine the influence of silicon on the position of the graphite solubility line. As seen in Fig. 19 of the present paper, the solubility at 900 to 950 degrees Cent.

[1]Becker, *Journal*, Iron and Steel Institute, 1925, No. 2, p. 239.

(1650-1740 degrees Fahr.) appeared to be much lower than expected and it is therefore interesting to see that in Experiment 9, Dr. Schwartz seems to confirm the low value. As a result of later work, the writer has no hesitation in saying that the low values at these temperatures did not represent the true solubility of carbon in iron, although there is no doubt that the iron specimens reached equilibrium with the gas surrounding them. Dr. Schwartz suggests that the low values may be due to the influence of oxygen in some form, but the writer favors the view that the gas probably never reached true equilibrium with the graphite present, because of the slowness of the reaction at these temperatures coupled with the effect of the reverse reaction occurring in the cooler parts of the furnace. The same explanation might account for the lower result obtained in Experiment 9 of the present paper.

Some years ago the writer conducted a series of experiments somewhat similar to those now recorded by Dr. Schwartz, but utilizing rather less pure material. The results were not published but it is satisfactory to note that the conclusion as to the metastability of cementite is in agreement with that now reached by the author. At the time, however, it was considered that the conclusion was not decisive owing to the very long annealing periods involved, the difficulty of accurately determining combined carbon content in the presence of free carbon, and the deceptiveness of microscopic evidence.

In order to avoid the difficulties mentioned, the writer adopted a different method, namely that involving the measurement of the ratio of carbon monoxide to carbon dioxide in equilibrium with cementite (white cast iron) on the one hand and graphite on the other. An account of this work has been published[2] and it should be noted that the line denoting equilibrium with cementite is perfectly distinct from that with graphite, while there is no indication that the two lines would cross even if extrapolated for some distance beyond the temperature range of the experiments. The results obtained by Johansson and von Seth, quoted by the author, are not entirely in accord, but in the particular method used by these investigators, slight errors in gas analysis would account for the lack of concordance. On the other hand the accuracy of the writer's results have since been confirmed by Bramley and Lord.[3] Dr. Schwartz appears to have overlooked these data and the writer feels justified in drawing attention to them because, in his opinion, they constitute the most decisive evidence supporting the conclusion as to the metastability of cementite.

Written Discussion: By Anson Hayes, Director Research Laboratories, American Rolling Mill Co., Middletown, Ohio.

There is only one phase of Dr. Schwartz' paper upon which I shall make comment; it concerns the double $A_{3.2.1}$ line of his Fig. 19 (the section on the iron-carbon diagram). In the TRANSACTIONS of the American Society for Steel Treating, May, 1927, page 767, Dr. Schwartz published under the title, *"Notes on the A_3 Stable Transformation,"* data to support his contention that there is a stable A_3 point which he considered was located at a temperature very near that of the A_2 point, and which he considered distinct from the usual A_3 point located in the pure iron system at about 900 degrees Cent. (1650 degrees Fahr.). Because of the incompatibility of such a concept with

[2]Becker, *Journal*, Iron and Steel Institute, 1930, No. 1, p. 337.
[3]Bramley and Lord, *Journal*, Chemical Society, 1932, p. 1641.

the recognized laws of solutions, I presented at that time a detailed interpretation of these laws with respect to the existence of a stable and a metastable $A_{3.2.1}$ line. This discussion may be found beginning on page 771 of the volume of the TRANSACTIONS cited above.

Dr. Schwartz has for a number of years postulated two solid solutions: one resulting from the solution of iron carbide in gamma iron; the other from carbon. This, we understand, is his reason for drawing the two $A_{3.2.1}$ lines in Fig. 19 of the present paper.

Attention should be called to one important requirement of the generally accepted laws of solutions: No matter how many forms of a solute may exist in a solution, if these forms of solute are in equilibrium with each other, there is only one freezing point line along which solvent-rich phase separates.

For the sake of illustration, consider the water-ferric chloride binary system. There are the following hydrates of ferric chloride:

$$FeCl_3 . 6H_2O$$
$$FeCl_3 . 3\tfrac{1}{2}H_2O$$
$$FeCl_3 . 2\tfrac{1}{2}H_2O$$
$$FeCl_3 . 2H_2O$$

Suppose a series of solutions from these various hydrates be made up in water, all conforming to the concentration 10 per cent by weight of $FeCl_3$. Experimental investigation of this system shows that no matter from which of the hydrates of ferric chloride the 10 per cent solution of $FeCl_3$ in water is obtained, the solvent, water, will begin separating from the solution at the same temperature, namely at about −8 degrees Cent. Dr. Schwartz' double $A_{3.2.1}$ line is equivalent to assuming in such a system that water would freeze out at slightly different temperatures, depending upon which form of salt was used to make up the same concentration of solution with respect to $FeCl_3$.

In order to justify the double $A_{3.2.1}$ line, it would, therefore, become necessary to show: (1) That the two forms of solute resulting from iron carbide in one case and from carbon in the other, are different, (2) That if these two solutions are different, the two forms of solution which do result from dissolving iron carbide in one case and graphite in the other, in gamma iron are not in equilibrium with each other.

One should keep in mind the fact that it is solvent which is separating from solid solution along the $A_{3.2.1}$ line rather than solute.

In view of the absence of adequate proof of the existence of two distinct types of solid solution—one from carbide and the other from graphite— and necessarily due also to the lack of proof of two such forms of solute not being in equilibrium with each other, the drawing of a double $A_{3.2.1}$ line seems unwarranted. The writer knows of no cases of solutions where different forms of the solute have been shown to exist out of equilibrium with each other, at concentrations where transformations are accompanied by separation of solvent-rich phase.

There is, of course, sufficient evidence to justify two solubility lines: one for the solubility in gamma iron of iron carbide (the A_{cm} line); the other for graphite (the graphite solubility line). That the gamma iron solid solution from either of these solutes may be reversibly converted into graphite and ferrite in one case, or into ferrite and cementite in the other, is common knowledge

and strongly suggests the presence of a mechanism by which equilibrium between any possible different forms of solute may be established. The slightly higher temperature for the ferrite graphite eutectoid is to be expected. This is because the stable eutectoid occurs at the intersection of the graphite solubility line with the $A_{2,2,1}$ line and lies to the left of the metastable A_{cm} line.

Written Discussion: By N. A. Ziegler, Power Use Research Department, West Penn Electric Co., Pittsburgh.

In connection with this very interesting paper, I would like to relate my experience with the instability of cementite, which, unfortunately enough, I cannot substantiate by any photographs.

Some two years ago I gave to my students in the metallography course at the night school of Carnegie Institute of Technology, some high carbon iron ingots, resulting as a by-product in my method for the analysis of gaseous elements in metals. (American Electrochemical Society, 1932). These ingots were composed of electrolytic iron melted in Acheson graphite crucibles in a vacuum of about 0.001 millimeters of mercury, and saturated with carbon to about 5-6 per cent. They were little disks about 1 inch in diameter, and ¼-½ inch thick. Their usual structure was a pearlitic matrix with a large quantity of graphite flakes, uniformly distributed throughout the entire material. Free cementite was present more or less accidently in very small amounts. This material usually could easily be cut with a hand saw. In one of these samples, however, a central hard spot was discovered. In fact, several saw blades were broken in the attempts to cut through it, and finally this sample had to be fractured with a chisel. When a surface of this sample, taken through the hard spot, was polished, it became obvious that a particle of about 2 millimeters in diameter, different from the surrounding material, was there present. It was so much harder than the surrounding material, that it stood in relief and could easily be observed with the unaided eye. When etched in nital and examined under a microscope, it became evident that this was an exceptionally large particle of massive cementite. It was brilliantly white, with cleavage lines distinguishable on its surface.

This sample was kept in a dessicator at room temperature for one or two weeks. When, after that period of time, it became desirable to examine this sample again, to our surprise we could not find any cementite; the outline of what formerly was the hard spot still could be plainly seen by the unaided eye, as well as under the microscope, but cementite was completely graphitized into very fine graphitic particles imbedded into a matrix of free ferrite, the surface of the latter being very rough.

This is a further evidence of the instability of the free cementite. When present with a large excess of iron, as in steels or cast iron, it can exist as Fe_3C for perhaps indefinite periods of time, but when isolated into large masses, as in this particular case, it has a tendency to graphitize even at room temperature.

The other factors determining the relative stability of cementite are: (1) presence of other elements in the alloy, which is a well known phenomenon; (2) external pressure: it is possible that the above described piece of cementite could exist as Fe_3C for an indefinite period of time, if left undisturbed inside of its parent ingot.

J. B. AUSTIN:[4] On page 149 of his paper Dr. Schwartz has given a conclusion as follows:

"It is concluded that direct experiment contradicts the thermodynamic deduction of Yap, Chu-Phay that cementite is metastable at temperatures lying above some undetermined value somewhat in excess of A_1." That statement as it stands is correct, but there is a possibility that people who are not acquainted with thermodynamic calculations may read in it an implication that the fault was in the thermodynamic deductions. The emphasis should not be on "the thermodynamic deductions" but on "the deductions of Yap," for Yap's conclusions result from his peculiar and arbitrary selection of data. I think it is safe to say that his views are not supported by the majority of those who have considered this question from a thermodynamic point of view, nor are they consistent with the best evidence. It is quite true, of course, that errors in judgment can be made in most thermodynamic calculations. In the majority of cases they will not seriously alter the final conclusion, but unfortunately in the present case the calculations are quite sensitive and the result is appreciably altered by the selections made.

The total of the thermodynamic evidence available in this question gives a definite indication that cementite is unstable at all these temperatures. It seems to me, therefore, that Dr. Schwartz's work is a confirmation of the thermodynamic predictions; and it is rather a pity that he did not mention the fact that thermodynamic deductions of Becker, Bramley and others indicate that cementite is unstable with respect to graphite at all the temperatures considered.

A. B. KINZEL:[5] I think that most of us who have followed certain of the thermodynamic calculations are impressed with the fact that not only is judgment involved, but also the selection of data is a very critical function as far as results are concerned. The differences of comparatively few degrees in temperature or tensile per cent of composition will frequently be sufficiently magnified in the calculations so as to lead to results that are not in accordance with facts as later proved.

JOHN CHIPMAN:[6] I am particularly sorry that Dr. Schwartz is not here. In his remarks on the thermodynamics of the situation, Dr. Schwartz has elaborated upon many entirely unimportant points which are only indirectly related to the problem in hand and which might better have been omitted. He overlooks almost entirely a great mass of thermodynamic data that is available in the literature. To my knowledge, there are at least eight pieces of research on equilibrium of cementite and gaseous mixtures, either carbon monoxide-carbon dioxide or methane-hydrogen mixtures. Each of these researches gives us quite directly a value of the free energy of cementite, independent of the useless details so elaborately discussed by Dr. Schwartz, both in his paper now and in the one he wrote in 1931. Of these researches, one must be discarded on account of faulty temperature measurements. A second is subject to grave doubts on account of the crudity of experimental details. This second one was selected by Yap for his thermodynamic calculations and it should be noted that it is the only one of the eight that could have lead to the conclusions which he reached. Dr. Schwartz is to be commended for his refusal to accept

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[5]Union Carbide and Carbon Research Laboratories, New York.
[6]Department of Engineering Research, University of Michigan, Ann Arbor, Mich.

Yap's conclusion, and in this regard, I believe that all physical chemists who are conversant with the subject will agree with Dr. Schwartz. The other six of the eight researches which I mentioned are unanimous and emphatic in demonstrating that cementite is metastable with respect to graphite and an iron phase at all temperatures. The graphitization of essentially silicon-free alloys by Kinzel and Moore and by Schwartz is confirmation of this thermodynamic deduction.

Author's Closure

The author is indebted to Dr. Becker for correcting an error in the bibliography referring to the latter's work. The titles of two of Dr. Becker's papers had unfortunately been confused.

It is also pleasant to learn of the fact that Bramley and Lord's investigations confirm on the basis of gas reactions the metastability of cementite at all temperatures; the details of this piece of work had not come to the writer's attention.

While not unmindful of the fact that the peculiarity observed by Dr. Becker and confirmed by the writer with regard to a very low carbon solubility in gamma iron in the stable system might be due to different equilibria at different temperatures in different parts of the same container, it seems to the writer that direct evidence is such as to point to the fact that if this be the explanation then this phenomenon manifests itself also by the oxidation of iron.

The author is not altogether in accord with Dr. Becker that a problem of this kind is best attacked by determinations of the CO-CO_2 equilibria. It is, of course, entirely correct that these equilibria are a perfect criterion of the relative stability of the two phases cementite and graphite. The experimental procedure is, however, so hedged about with difficulties that apparently many quite skillful workers have been led to publish observations which contradict the writer's conceptions of the stability conditions, which conceptions are apparently shared by Dr. Becker. It is precisely because apparently incorrect conclusions have been drawn from data of this type that the writer undertook the present investigation. The fact that certain particular workers are skilled enough to get the correct results and confirm the independent observation of metastability is, of course, gratifying but still does not overcome the difficulty that the student who does not know which result is right would find considerable difficulty, as Yap did, in deciding upon which series of gas analyses to accept.

Dr. Hayes discusses the question of whether or not there exist two critical points or one marking the A_3 transformation. It happens that the author did not touch upon this point in the paper now under discussion and it seems inadvisable to enlarge upon Dr. Hayes' comments except to point out that had he examined the author's Fig. 19 carefully he would have seen that the two lines are suggested or perhaps better, computed not by the writer but by Körber and Oelsen and are included as an expression of their views and not those of the present author. It may be added that in the research now in question it had been hoped to locate quite accurately the lower end of the A_{cr} line but the experimental results did not finally warrant any such discussion.

(Discussion—Continued on Page 285)

HEAT TREATMENT IN CONTROLLED ATMOSPHERES INCLUDING GASEOUS CARBURIZING

By C. R. Austin

Abstract

Considerable attention has been given to various aspects of controlled atmosphere heat treatment during the past few years. In the present paper the author attempts to present a general discussion of the application of batch type anneal or continuous normalizing to low carbon steel, stainless steel, copper, brass and silicon steel. Attention is drawn to the more important fundamentals which must be considered, and examples of annealing practice are provided.

A theoretical discussion on the anneal of high carbon steels in carbon-bearing gases indicates the relative importance of such factors as "carbon-concentration" in the atmosphere, time diffusion (conveying of carbide away from the gas-metal interface) and diffusion of carburizing gases into the metal. The need for correlation with the Acm line of the equilibrium diagram is emphasized.

The practical heat treatment of these steels is illustrated by photomicrographs or data on carbon analyses under the following subheadings:

1. *Surface carburization of low carbon steels.*
2. *Surface recarburization of high carbon steels.*
3. *High carbon steel anneal in pure dry hydrogen.*

MUCH has been written during the past three or four years on the heat treatment of metals in controlled atmospheres and special attention has been devoted to gas carburizing. Almost a dozen articles have already appeared in *Metal Progress,* and in the present paper the writer intends to discuss some general aspects of this subject with which he has been closely associated for several years.

The usual purpose of a controlled atmosphere during a heat treatment cycle is to protect the surface of the metal so that it shall remain unoxidized. It is also frequently required that the surface shall be cleaned free from color resulting from preoxidation of the metal,

A paper presented before the Sixteenth Annual Convention of the Society held in New York City the week of October 1, 1934. The author, C. R. Austin, a member of the Society, is associate professor of metallurgy, Pennsylvania State College, State College, Pa. Manuscript received July 24, 1934.

occurring during an earlier stage in fabrication. This applies to low carbon steel such as tinplate and automobile body sheet, stainless steels, copper and brass, where considerable economy can be effected by the partial or complete elimination of the pickling bath.

In annealing high carbon steel such as razor blade stock, file blades and hack saw material it is desirable to keep the surface free from oxidation in order to prevent surface decarburization, and even perhaps, to supply carbon to the surface of the steel if partial decarburization has occurred during hot rolling, or other shaping operation.

The bright annealing of stainless steel is a problem of considerable difficulty and may be extremely difficult to realize commercially.

Electric sheet or silicon steel also presents a field for the application of the principles of bright annealing but here the problem relates rather to the reduction of oxygen and carbon content of the alloy and to the elimination of strain than to the production of a bright sheet or punching. A smooth surface finish however is desirable.

Low Carbon Steel

Theoretically the bright annealing of low carbon steel is a simple operation in which the atmosphere during annealing must be neutral or reducing depending on the surface of the metal as charged into the furnace. Many different gases have been used for this purpose such as coke oven gas, natural gas, and dissociated ammonia. It is important that the gas be not more than slightly carburizing if a hydrocarbon gas is used, and that any atmosphere should not contain any free oxygen. Considerable amounts of water vapor may be present if the gas is thoroughly reducing, without oxidation of the annealed product.

Much low carbon steel is annealed on the batch anneal principle. For this purpose the bell type electric furnace appears to have marked advantages over the conventional anneal gas-fired furnaces due to improved quality of product depending on better heat distribution and easier control of atmosphere. Better heat insulation, reduction in total time of annealing cycle, and the small differential between the temperature of the heating medium (electrically heated coils) and the charge are also important factors.

In order to obtain a completely bright product it is necessary that consideration be given to the condition of the surface of the

charge prior to the heat treatment, and to insure that the atmosphere does not contain free oxygen during the cooling end of the cycle. The simplest chemical reactions which occur during anneal are as follows:

$$4Fe + 3O_2 \rightleftarrows 2Fe_2O_3 \quad (1)$$
$$2H_2 + O_2 \rightleftarrows 2H_2O \quad (2)$$
$$Fe_2O_3 + 3H_2 \rightleftarrows 3H_2O + 2Fe \quad (3)$$

At red heat and above reactions (2) and (3) takes place very readily in the left to right direction. Hence iron oxide is reduced to the metallic state and free oxygen is reduced to water vapor. During the cooling cycle however the affinity of oxygen for iron at 400 to 500 degrees Cent. (750-930 degrees Fahr.) and below is greater than for hydrogen so that if any free oxygen is present in the gas discoloration of the charge takes place according to equation 1. Considerable amounts of water vapor must be present before the reaction given by equation 3 leads to the formation of iron oxide and free hydrogen. The equilibrium conditions in this instance are well known and are dependent on temperature.

In continuous furnace annealing the rigorous conditions as regards absence of free oxygen are not so necessary since rapid cooling through the 400 to 500-degree Cent. (750-930 degrees Fahr.) range is effected. At lower temperatures the oxidation is so slow with low oxygen concentrations that it is not readily detected. Experiments have shown that a few parts per million of free oxygen in hydrogen gas passed over steel strip will cause discoloration of the metal in a short time. In fact this phenomenon can be used to purify hydrogen by passing "pure hydrogen" over steel heated to this temperature range since it provides a simple means of removing the last traces of free oxygen.

An example of the bright annealing of cold-rolled sheets in a batch-type furnace is shown in Fig. 1. The anneal was conducted in a dissociated ammonia atmosphere on stacked sheets having the usual oil film on the surface of the sheet, as taken from the cold rolls. The temperature of the charge was raised to 675 degrees Cent. (1250 degrees Fahr.) in about 12 hours followed by a cooling rate of about 17 degrees Cent. (30 degrees Fahr.) per hour from 675 degrees Cent. (1250 degrees Fahr.) to 205 degrees Cent. (400 degrees Fahr.). The type of furnace illustrated has been frequently described. It consists of a base, carrying the charge, over which is placed a metal hood which forms a gas-tight chamber by virtue of an

oil seal around the periphery of the base. A bell lowered over the hood serves to furnish the thermal energy by means of the electrically controlled conventional nickel-chromium heating elements hung on the inside of the bell.

Considerable quantities of oil distilled off from the charge during the passage of the dissociated ammonia gas as the charge heated

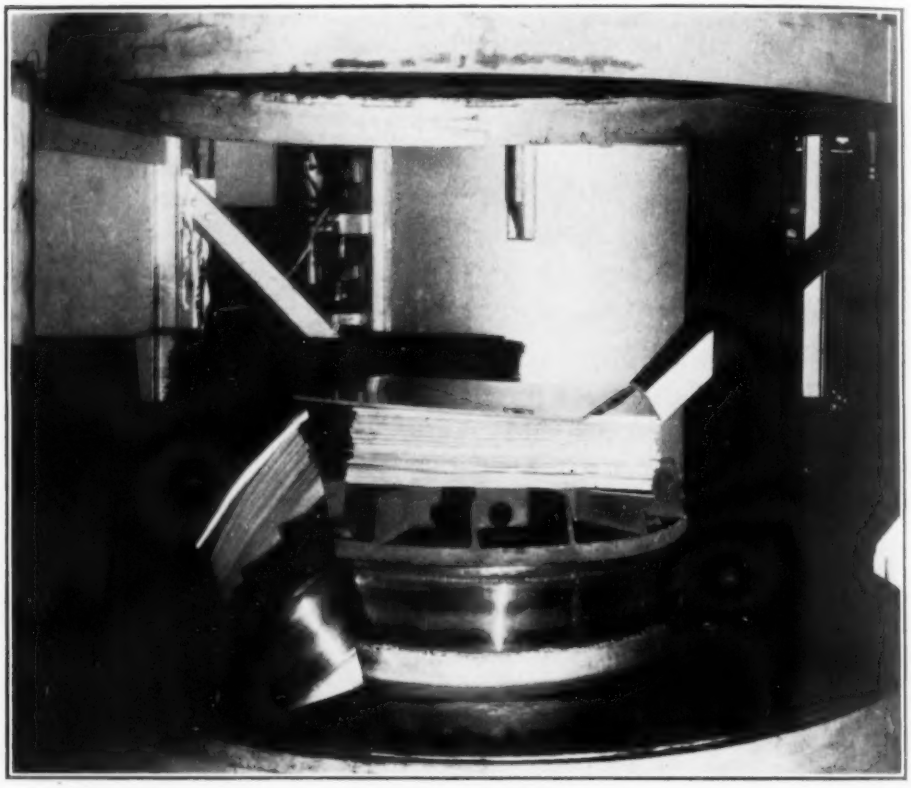

Fig. 1—Bright Anneal of Cold-rolled Sheet in a Bell-type Electric Furnace Using Dissociated Ammonia as the Controlled Atmosphere.

up, but since clean oil was used in the cold rolling it can be observed that a true bright anneal was effected. Reflections on the annealed sheet demonstrate the nature of the surface.

Low carbon wire rod, coils of strip and tinplate have been successfully annealed by this method where especial importance is accorded surface finish and uniformity of product (anneal). Annealing can also be effectively accomplished by a continuous treatment whereby the product is passed through the furnace in a continuous strip form or on conveyors. In this case the gas consumption used to maintain a controlled atmosphere is usually considerably greater but since the temperature cycle is much reduced it is not gen-

erally necessary to so rigidly maintain gas purity and frequently a cheaper gaseous atmosphere may be employed.

Continuous furnace treatment in controlled atmospheres has been used for rapid bright normalizing low carbon steel sheet and for tinplate. Data from some experimental work in this field may be of interest. In simulating the conditions obtaining in continuous normalizing, sections of 0.1 per cent carbon steel sheet about 20 inches long by 10 inches wide were thrust into the hot zone of a long muffle containing the desired atmosphere, maintained there a predetermined period, rapidly withdrawn to a water-cooled section of the muffle to cool rapidly and finally withdrawn completely for examination. The photomicrographs in Fig. 2 demonstrate the rapidity with which complete normalizing can be effected. After 3 minutes at 950 degrees Cent. (1740 degrees Fahr.) the banding found in the rolled structure was completely eliminated. Evidence of the hot-rolled structure persists after 1 minute at 940 degrees Cent. (1725 degrees Fahr.) but a very good normalized microstructure results from 4 minutes at 930 degrees Cent. (1705 degrees Fahr.). Even with partially oxidized sheet the dissociated ammonia atmosphere employed in this work provides a satisfactory bright annealed sheet within the time limits employed.

To examine the effectiveness of the heat treatment on the deep drawing properties of the material several of the normalized sheets were tested in the Erickson machine. Table I.

Table I
Erickson Tests on Sheet Steel

	Normalizing Temperature		Time at Temperature in Minutes	Erickson Value Millimeters
	Degrees Cent.	Degrees Fahr.		
3	960	1760	1	8.94-8.81
4	960	1760	1	9.40-9.04
5	960	1760	2	8.53-8.65
6	960	1760	5	8.66-9.15
7	950	1740	3	8.86-8.72
8	930	1705	4	8.56-9.04

The Erickson value desired was 10.50-11.00 millimeters. It may be noted that the variation in time and temperature does not have marked effect on the Erickson value. This was also true of directional properties. There is little doubt that the relatively low values recorded are due to rapid rate of cooling after passing through the critical range. Slower rate critical cooling is desirable for deep drawing purposes. It should be noted that the surface of

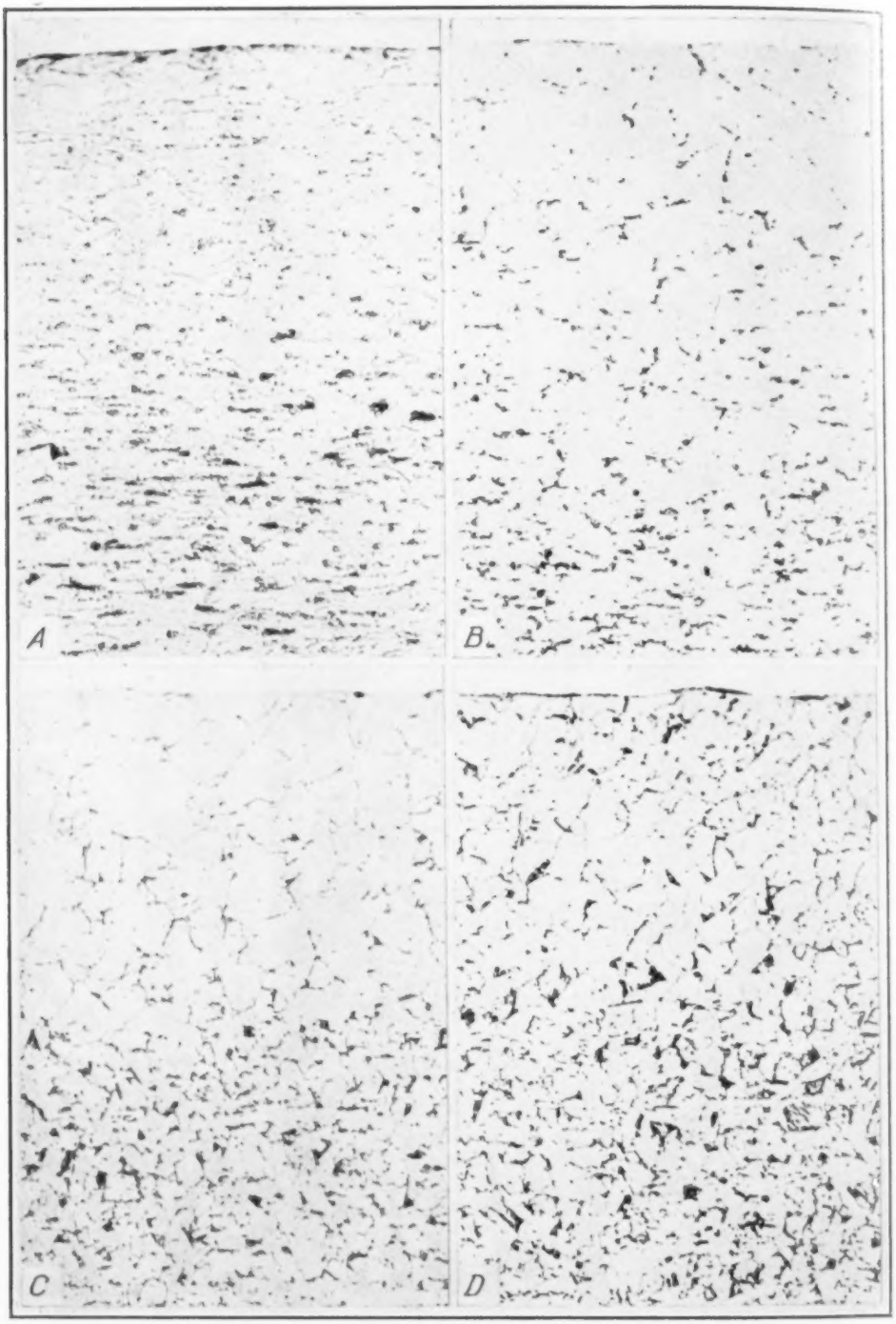

Fig. 2—Microstructures of Rapid Continuous Bright Normalizing of Steel Sheet in a Dissociated Ammonia Atmosphere.

A. As Received in Hot-rolled Condition.

B. Normalized for 1 Minute at 960 Degrees Cent. (1760 Degrees Fahr.).

C. Normalized for 3 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.).

D. Normalized for 4 Minutes at 930 Degrees Cent. (1705 Degrees Fahr.). All Photomicrographs × 200.

the sheets were decarburized. Further reference will be made to this in the section dealing with high carbon steels.

Much thought has been given to the bright annealing of tinplate particularly with a view to elimination of one or more of the pickling operations. A peculiar feature attaches to this problem however, since the tinplate manufacturer is concerned with the familiar patterns found on tinplate when stripped from the pack. Much of this pattern, including the speckling known in the trade as "egg-shell" pattern, is removed by pickling, but it tends to persist if the sheet is subjected to bright annealing whereby the oxidized portions of the sheet are reduced to metallic iron. This is a real problem confronting the application of bright annealing to the later stages of tinplate manufacture where the surface appearance of the tinned product is of paramount importance. Preoxidation of the complete sheet prior to bright annealing, in an effort to eliminate the surface patterns, has been attended with moderate success.

Stainless Steel

Stainless steels contain varying amounts of chromium which renders the true bright annealing of such steels extremely difficult in commercial practice. In a recent paper by the author[1] on the role of water vapor in decarburization the writer indicated the extreme sensitivity of chromium alloys to oxidation discoloration at elevated temperatures in a reducing hydrogen atmosphere. This is due to the presence of minute amounts of free oxygen or oxygen-bearing gases (including water vapor). It is generally considered that chromic oxide is reduced to the metallic state by the hydrogen only at extremely high temperatures. This is not true for reduction can be effected between 700 and 800 degrees Cent. (1290-1470 degrees Fahr.) in pure hydrogen which has been subjected to some special purification process whereby the hydrogen contains less than one part per million of water vapor. Definite data on the exact purification required cannot readily be determined experimentally on account of the difficulties involved in the chemical analysis, either direct or indirect.

By setting up suitable purification trains the bright annealing of tarnished stainless steel has been accomplished on an experimental basis. It is difficult to conceive however that this can be

[1] C. R. Austin, "A Study of the Effect of Water Vapor on the Surface Decarburization of Steel by Hydrogen with Certain Developments in Gas Purification", Transactions, American Society for Metals, Vol. 22, No. 1, Jan., 1934, p. 31.

economically conducted in commercial practice. Brief reference is made to this subject by Pierce and Grossmann in the recent "Book of Stainless Steels" where they discuss the surrounding of the material by special gases "as in bright annealing." They further state that the artificial atmosphere prevents the formation of scale altogether. Obviously tarnishing of the product is not prevented.

It would therefore seem that true bright anneal of stainless steels is at present commercially impracticable and that the fabrication of sheet with a lustrous finish must depend on the elimination of scaling by use of a reducing atmosphere during heat treatment followed by a suitable pickling operation to remove oxidation films causing the familiar discoloration of chromium alloys. Considerable care is necessary in pickling, when a brilliant lustre is desired, and a passivating action in nitric acid is used to prevent etching of the metal surface.

It would appear that the application of the Bullard-Dunn pickling process, where a slight lead deposit preserves the metal surface from attack, might prove helpful in the processing of stainless steel.

Copper and Brass

The "bright annealing" of certain copper products has been conducted by the continuous annealing method, using water seals at each end of the heated muffle, for several years. Interest in the true bright annealing of fabricated copper such as refrigerator coils has led to experimental tests on bell furnace anneals in various gas atmospheres. While hydrogen appears to be the logical gas for this purpose the use of ordinary commercial copper may prohibit this on account of hydrogen embrittlement. The use of oxygen-free copper now on the market eliminates the difficulty.

With the ordinary commercial copper successful bright anneals in the electric bell-type furnace have been obtained in various controlled atmospheres including nitrogen, steam, natural gas and butane. With nitrogen and steam the product must be charged into the furnace in a bright condition and both gaseous media must be treated for the removal of free oxygen. With nitrogen this may readily be accomplished by first passing the gas through a tube of copper, held at a low red heat, which is periodically reduced to the metallic state by use of hydrogen for the purpose of maintaining its efficiency. In order to render the steam completely non-oxidizing it is first necessary to boil off to the atmosphere a small quantity of

the water initially placed in the boiler. This removes all free oxygen from the water. Further, it is desirable to replace the steam with some non-oxidizing gas (pure nitrogen or tank hydrogen) toward the end of the cooling cycle and before the temperature falls to 100 degrees Cent. (212 degrees Fahr.). This procedure of course prevents the condensation of water on the annealed product, thus eliminating water stains.

Annealing in an atmosphere of butane gas has proved successful in bright annealing bright finished copper and surface oxidized copper, at temperatures up to 510 deegrees Cent. (950 degrees Fahr.). Reduction of any oxide tarnished surface has been effected without any apparent hydrogen embrittlement and evidence of sooting could not be detected. It is possible that the tendency to embrittlement of tough pitch copper may be markedly reduced by the use of hydrocarbons instead of free hydrogen, assuming that the hydrocarbon as such, possesses reducing powers for copper oxide and does not appreciably pyrolyze at the annealing temperature employed. This decrease in embrittling effect would then be explained on the theory that the heavy hydrocarbon molecule, although causing surface reduction, is too large to permit much diffusion in copper.

The bright anneal of brass is a much more difficult problem particularly for the reason that zinc volatilization readily occurs. The loss of zinc per se is not so serious but its effect on the surface of the alloy may be very marked. Furthermore, slight surface oxidation is more readily noted on brass than on copper due to the white color of the zinc oxide formed. The effect of composition, temperature of anneal, and previous rolling history is also extremely important in its influence on grain-size, and the control of grain-size is important in the technique of brass manufacture.

In general, and this refers particularly to brass, the greater the amount of cold work put into the alloy before annealing the simpler the bright annealing problem since the temperature of anneal is progressively lowered as the work hardening increases. Oxidation and volatilization difficulties are thereby reduced. Thus in batch annealing it is important that uniform temperature distribution be maintained throughout the charge so that the product responds uniformly to the hardening effect in the cold rolls. Maximum hardening can thus be obtained throughout the charge with subsequent minimum temperature of anneal for complete softening. Incidentally this can lead to important saving in the power consumption for

rolling. The most important reason for annealing brass in controlled atmospheres, however, depends on the economic saving possible in the elimination of certain pickling operations.

From the foregoing comments it can be seen that the bright anneal of brass is a complex problem. It should also be stated that the term "bright anneal" as applied to this alloy usually infers an anneal which provides a surface finish comparable to the characteristic appearance associated with cold-rolled brass which has previously been thoroughly cleaned by pickling. Very little chemical reduction can therefore be permitted in the bright annealing operation and a clean product should be charged into the furnace. The problem is then essentially one where the important factors are:

1. A neutral or reducing atmosphere to prevent surface tarnish by oxidation.
2. A temperature sufficiently high to produce complete softening, due regard being paid to control of grain-size.
3. The prevention of zinc volatilization.

Thorough work hardening before anneal permits a lower annealing temperature to be used, and this in turn assists in minimizing the loss by zinc volatilization. It is reported that considerable headway has been made in England with regard to the third factor by introducing zinc vapor into the furnace atmosphere to counteract the zinc volatilization due to the relatively high vapor pressure of zinc at low temperatures.

Cowan[2] has made an interesting observation on the anneal of commercial brass. He states that on heating brass and pure hydrogen together at 430 degrees Cent. (805 degrees Fahr.) tarnishing occurred due to gas evolution from the brass. This tarnishing persisted until the temperature was raised to 680 degrees Cent. (1255 degrees Fahr.). Referring to the importance of differentiating between temperature of the metal and temperature of the gas, and this is particularly important in continuous annealing operations, Cowan adds that if the atmosphere were maintained at 680 degrees Cent. (1255 degrees Fahr.) the brass could be passed through a furnace in such a way as never to attain a temperature higher than 430 degrees Cent. (805 degrees Fahr.) without any indication of tarnishing. Much remains to be done in the development of the true bright anneal of brass.

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[2]R. J. Cowan, "The Chemical Effect of Gaseous Atmospheres in Bright Annealing of Metals", *Metal Industry*, August, 1931.

Silicon Steel

In recent years much attention has been given to the effects of grain-size and impurities on the magnetic properties of silicon steels and Yensen and Ruder have contributed valuable information on the subject. This has led to the recognition of the importance of the application to silicon steels of controlled atmosphere anneal whereby the carbon-oxygen content of the alloys can be maintained low or even reduced during the annealing process. Some of the most interesting results have been obtained by annealing in pure hydrogen free from oxygen and water vapor except for the slightest traces, using the conventional long annealing cycle with a maximum temperature above 1000 degrees Cent. (1830 degrees Fahr.).

Fig. 3—An Experimental Charge of Silicon Sheet Stampings After Bright Annealing in Dissociated Ammonia.

For these high temperature anneals special attention must be given to refractories and heating elements (where electric heating is employed) on account of the disintegration of the refractories by hydrogen reduction and on account of the failure of nickel-chromium heating elements in a reducing atmosphere at such elevated temperatures. Other heating elements have proved superior for this purpose.

In experimental anneals on rings cut from 1 to 4 per cent silicon steel a slow annealing cycle (totalling 200 hours) was conducted in

air and in dissociated ammonia. Fig. 3. A maximum temperature of 1010 degrees Cent. (1850 degrees Fahr.) was maintained for 6 hours. Some of the steels had comparable magnetic properties under both conditions of anneal. The 2.5 and 3 per cent silicon samples showed marked improvement in the maximum permeability and in loss values when annealed in cracked ammonia gas. The dissociated ammonia apparently causes no embrittlement, permits the removal of the samples from the annealing box in a clean bright condition, and does not lead to any sticking troubles as the rings were separated without difficulty.

High Carbon Steels

Perhaps the annealing of high carbon steels presents some of the most interesting problems in the surface control of alloys during heat treatment, and probably this phase of the subject has attracted the attention of writers more than any other. Much research has been devoted to the subject, yet there does not appear to be complete agreement in the interpretation of results among such authorities as Cowan[3] Guthrie[4] and McQuaid,[5] and the writer here presents some observations culled from his own experience with the use of certain neutral and carburizing atmospheres.

It is proposed to give some attention to the theoretical aspects of the subject before illustrating results obtained in experimental analysis of the problems.

Theoretical Considerations

Whether the purpose of the heat treatment is to carburize a medium carbon steel, to prevent decarburization of a high carbon steel, or to raise the carbon content of the peripheral parts of a carbon steel (where decarburization has occurred) to a concentration equal to that of the core, the correct treatment is based on the same fundamental theory. Fig. 4.

Consider first the lines forming the eutectoid in any low carbon alloy. The maximum concentration of carbon which can be induced in the peripheral parts of the steel by carburization depends wholly on the temperature no matter what gaseous carburizing medium is

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[3]R. J. Cowan, "Continuous Carburizing by Gas", *Metal Progress*, Feb., 1932. R. J. Cowan, "Heating or Annealing", *Metal Progress*, Jan., 1934. R. J. Cowan, "Recent Progress in Gas Carburizing", *Metal Progress*, Oct., 1933.

[4]R. G. Guthrie, "Carbonization of Steel with Gas", *Metal Progress*, Nov., 1931.

[5]H. W. McQuaid, "Gas Carburizing", *Metal Progress*, July, 1934.

employed assuming, however, that the gas is maintained saturated with respect to carbon. Thus at temperature T the maximum carbon concentration obtainable by carburization is indicated by C. The temperature therefore is a definite criterion of *maximum* carbon content assuming we know the position of the Acm line E B of the particular steel under consideration.

The second factor, the carburizing atmosphere, determines whether this maximum concentration on peripheral sections may be

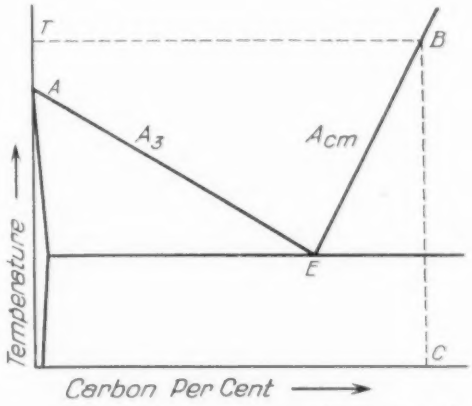

Fig. 4—Sketch of Eutectoid Portion of Iron-Carbon Diagram.

attained. Time-diffusion, a third factor, is the one which is mainly responsible for conveying the carbide (or carbon) away from the surface of the steel.

The effect of carbon concentration in carburizing gases has been discussed by Sykes.[6] Thus in the case of methane (CH_4) it is assumed that as the volume per cent methane in equilibrium with carbon and hydrogen by pyrolysis at 800 degrees Cent. (1470 degrees Fahr.) is 10.0 per cent, and as iron will hold in solid solution at 800 degrees Cent. (1470 degrees Fahr.) about 1 per cent carbon, then the vapor pressure of the carbon in this austenite should be equal to the vapor pressure of the carbon in the atmosphere $CH_4/H_2/C$ containing 10 per cent methane. This follows since both gaseous and solid components are completely saturated with respect to carbon, and there can be no tendency for interchange of the element between the two systems.

It is further assumed that at a given temperature the vapor pressure of the carbon in an austenite containing but one-half the

[6]W. P. Sykes, "Carburizing Iron by Mixtures of Hydrogen and Methane, TRANSACTIONS, American Society for Steel Treating, Vol. 12, Nov., 1927, p. 737.

carbon necessary for saturation is equal to the vapor pressure of the carbon in the $CH_4/H_2/C$ atmosphere in which the concentration of methane is one-half that required for equilibrium in the system. Thus carburization of a plain carbon steel at 800 degrees Cent. (1470 degrees Fahr.) in a $CH_4/H_2/C$ atmosphere containing 5 per cent methane by volume would lead to a maximum peripheral carbon content of 0.5 per cent. To summarize, the carbon in the steel surface may be controlled by the concentration of the hydrocarbon in the hydrogen atmosphere. Hence if high temperatures are used, where the rates of carburization and diffusion are rapid the maximum carbon concentration at the surface can be controlled by limiting the hydrocarbon addition to the hydrogen.

A fourth factor is the diffusion of the carburizing gas into the steel whereby the carbon is deposited in situ *within* the peripheral parts of the alloy. McQuaid[7] in a recent article casts considerable doubt on the possible mechanism of such a reaction and appears to consider that "atomic carbon" liberated at the gas-metal interface provides the only means of carbon interchange from gas to metal.

It is difficult to understand why the simple interface reaction (for methane)

$$3Fe + CH_4 \rightleftarrows Fe3C + 2H_2$$

should not be accepted. Further, there does not appear to be sufficient evidence to dismiss carbon monoxide as an extremely slow and poor carburizing gas, although the writer is in complete agreement with McQuaid's enthusiasm for the use of hydrocarbon gases for rapid carburization.

With regard to the diffusion of carburizing gases into the body of the steel the writer is not aware of any data which definitely answers this important point. On the question of decarburization it is believed that evidence was provided (in the author's cited paper[8] at the Detroit Convention 1933) to demonstrate the contention that decarburization is partly accounted for on the supposition that the carbon reaction takes place within the steel as well as at the gas-iron interface (see author's closure to discussion). The argument is based on the theory of Fick's law of diffusion.

Assuming that the experimental data correctly permitted the deduction outlined above there appears good reason to believe that the converse can hold true and that carburization by gaseous diffusion can occur.

[7]H. W. McQuaid, "Gas Carburizing", *Metal Progress*, July, 1934.
[8]loc. cit.

Practical Data on Carburizing and on Annealing High Carbon Steels

Discussion of the heat treatment in controlled atmospheres is to be concluded with data and illustrations under the following sections:

1. Surface carburization of low carbon steels.
2. Surface recarburization of high carbon steels.
3. High carbon steel anneal in pure dry hydrocarbon.

1. Surface Carburization of Low Carbon Steels

In the fabrication of low carbon steel sheet it is common to find that practically all the carbon has been removed from the surface of the sheet. This was recorded and illustrated in the first section of the paper. When it is required to galvanize the metal it is stated that this surface decarburization does not permit the production of a "tight coat," and hence it is desirable to recarburize slightly the surface layer.

In order to pursue the general trend of bright normalizing so as to eliminate pickling, experiments were conducted with a view to determining what success could be achieved by attempting to surface recarburize concomitant with rapid continuous type bright normalizing.

The sheet was introduced into the furnace for a pre-determined time and rapidly cooled in the manner described early in this paper. The atmospheres used included mixtures of butane gas and dissociated ammonia with and without additions of water vapor. The rate of recarburization was so rapid that it was decided to note the conditions under which ordinary carburizing could be effected up to an extent approximating the thickness of the sheet which was 0.040 inches.

The results are best shown by illustration, giving metallographic sections of sheets under various conditions. Fig. 5A-5D shows four different sections at 100 diameters of magnification.

Using dry dissociated ammonia-butane mixtures, very satisfactory surface recarburization was obtained with 2 per cent butane maintained 3 minutes at 960 degrees Cent. (1760 degrees Fahr.) and by 3.5 per cent butane at 945 degrees Cent. (1735 degrees Fahr.) for 3 minutes. With 6 per cent butane at 945 degrees Cent. (1735 degrees Fahr.) for 1 minute the peripheral carbon content appears to be in-

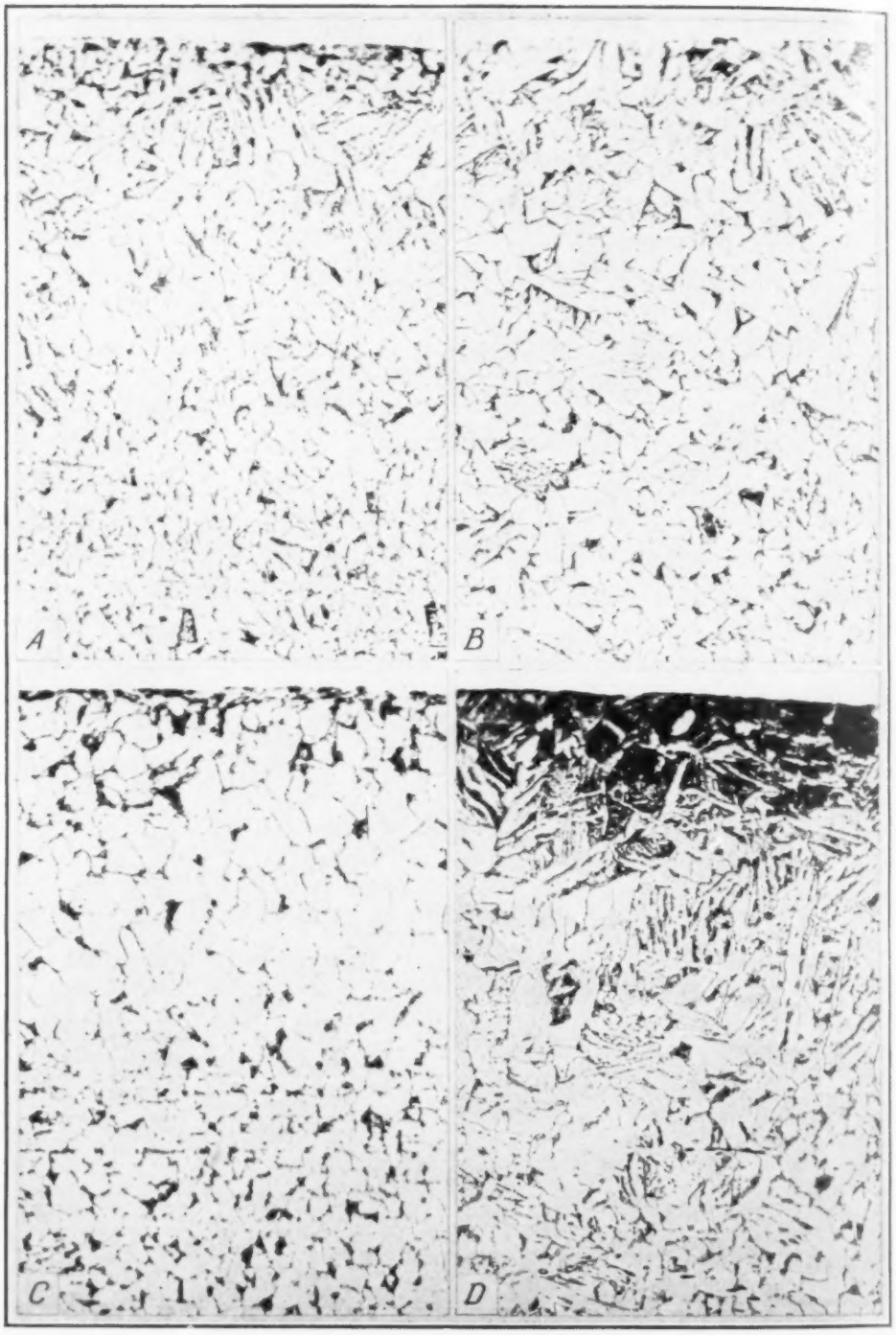

Fig. 5—Rapid Continuous Surface Recarburization of Low Carbon Sheet Concomitant with Bright Normalizing in Dissociated Ammonia Butane Mixtures.

A. Normalized in Dissociated Ammonia Containing 2 Per Cent Butane Maintained 3 Minutes at 960 Degrees Cent. (1760 Degrees Fahr.).

B. Normalized in Dissociated Ammonia Containing 3.5 Per Cent Butane Maintained 3 Minutes at 945 Degrees Cent. (1735 Degrees Fahr.).

C. Normalized in Dissociated Ammonia Containing 6 Per Cent Butane Maintained 1 Minute at 945 Degrees Cent. (1735 Degrees Fahr.).

D. Normalized in Dissociated Ammonia Containing 12 Per Cent Butane Maintained 3 Minutes at 965 Degrees Cent. (1770 Degrees Fahr.). All Photomicrographs × 200.

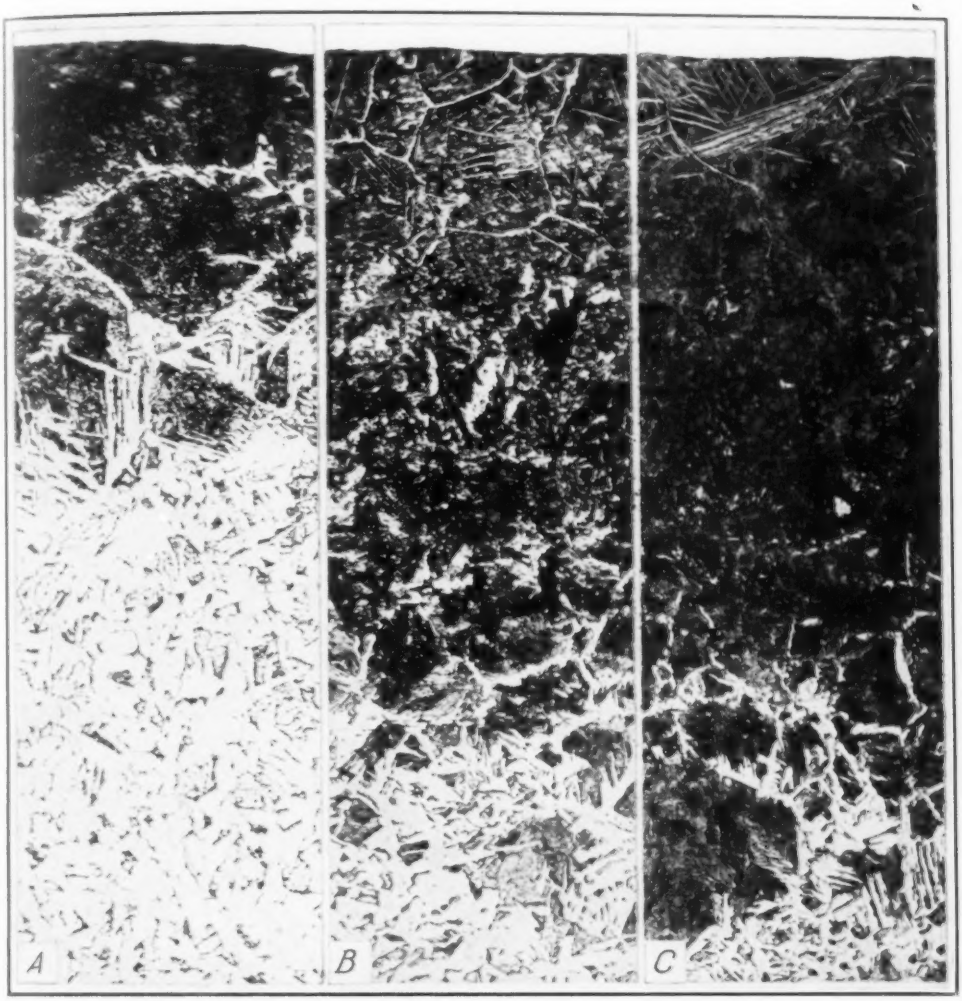

Fig. 6—Rapid Case Carburizing Under Conditions Simulating Continuous Bright Normalizing in Butane-dissociated Ammonia Atmosphere.
A. Maintained 15 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 8 Per Cent Butane.
B. Maintained 15 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 10 Per Cent Butane.
C. Maintained 20 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 10 Per Cent Butane. All Photomicrographs × 200.

creasing, but penetration was poor. Complete normalizing has not been effected since the directional effects of rolling are still evident. With 12 per cent butane for 3 minutes at 965 degrees Cent (1770 degrees Fahr.) a definite "case" is beginning to appear. The results of further increase in butane concentration, and time at temperature are also recorded by illustration in Fig. 6. With 10 per cent butane at 950 degrees Cent. (1740 degrees Fahr.) an extreme peripheral coat of hypereutectoid steel is observed after only 15 minutes. It

should be mentioned that the sheets were carburized on both surfaces. Sections showing the microscopic features entirely across the section of the sheet are also included. Fig. 7. All sheets were bright annealed or normalized concomitant with the surface carburization.

A theoretical study of probable reactions in this case depends primarily on the pyrolysis of butane more than on the physico-chemical laws of mass action. However, very little is known of the pyrolysis at temperatures below 600-700 degrees Cent. (1110-1290 degrees Fahr.), and there does not appear to be any available information on temperatures used in the metallurgical annealing operations herein considered. Furthermore, a change in space rate profoundly affects the products of pyrolysis. In the above tests soot deposit was very limited, especially in low butane concentrations.

In considering the possibility of inhibiting any soot deposition due to pyrolysis in dissociated ammonia-butane mixtures it was thought that water vapor additions would oxidize at least part of the free carbon. At the same time it was not certain what effect this addition might have on the bright annealing of the sheets. However, with the water vapor concentration obtained by saturating the dissociated ammonia at 70-80 degrees Fahr., no tarnishing was detected.

It has been stated that hydrocarbons have a much greater carburizing power in the presence of water vapor, and that the well known energizers used in carburization do not function unless they can be decomposed to liberate oxygen;[9] that is, form iron oxide or carbon-oxygen compounds.

In the present study it is believed that the moisture-bearing mixtures did carburize a little more rapidly than the dry gases (note 2 and 3.25 per cent butane for 3 minutes in pressure of water vapor). Fig. 8.

However, it can be stated that normalizing and surface recarburizing can be accomplished consistently in the space of a few minutes by use of dissociated ammonia-butane mixtures. Such an atmosphere also provides a satisfactory bright anneal.

2. *Surface Recarburization of High Carbon Steels*

It is common in the process of manufacture of high carbon steels to encounter surface decarburization. In general this may be serious due to the need for a hard cutting or abrading surface in

[9]G. M. Enos, "The Role of Energizers in Carburizing Compounds, TRANSACTIONS, American Society for Steel Treating, Vol. 20, No. 1, July, 1932, p. 27.

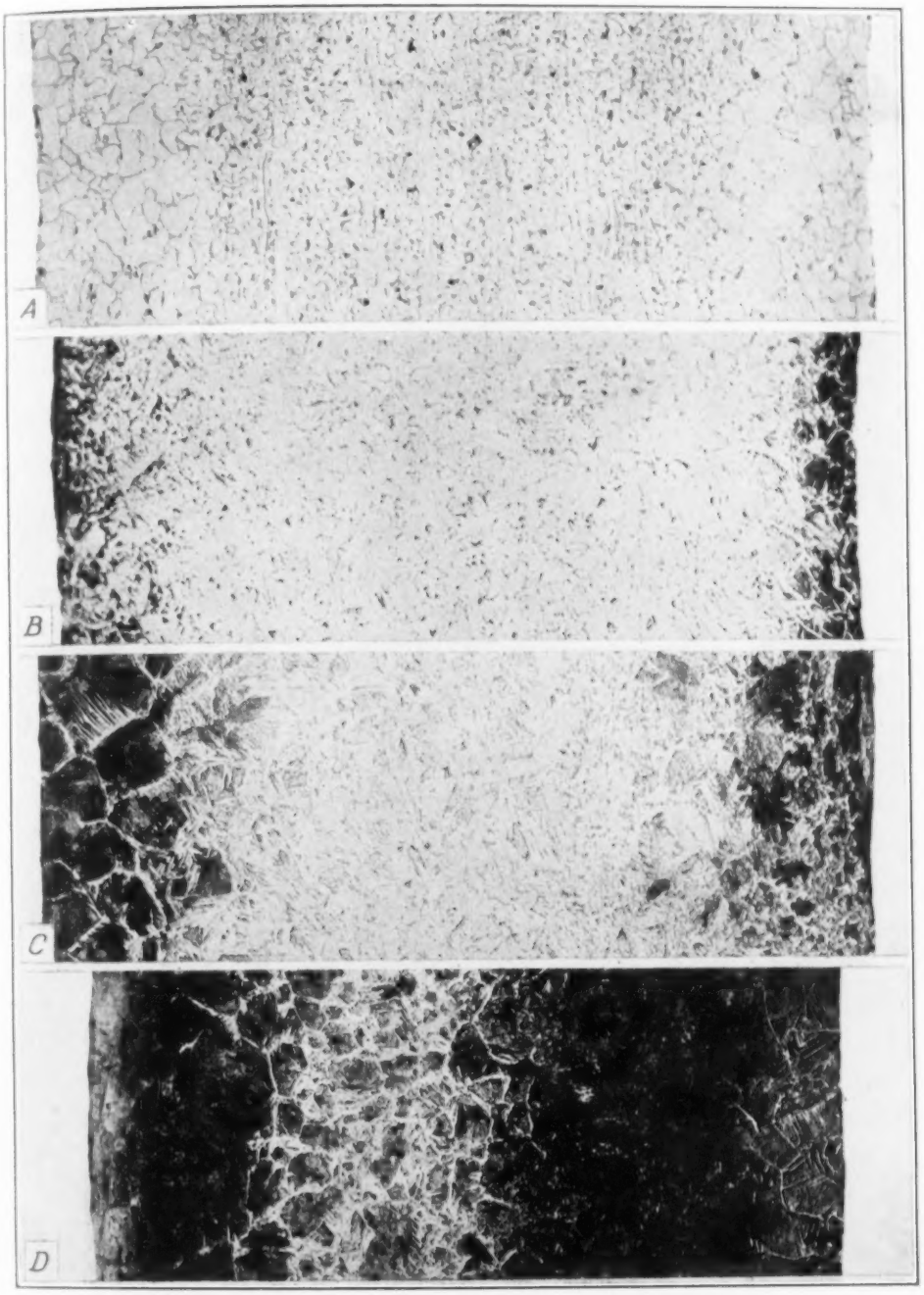

Fig. 7—Rapid Case Carburizing Under Conditions Simulating Continuous Bright Normalizing in Butane-dissociated Ammonia Atmosphere.

A. Normalized but not Subject to Carburizing Atmosphere.
B. Normalized 3 Minutes at 965 Degrees Cent. (1770 Degrees Fahr.) in Dissociated Ammonia Containing 12 Per Cent Butane.
C. Normalized 15 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 8 Per Cent Butane.
D. Normalized 20 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 10 Per Cent Butane. All Photomicrographs × 100.

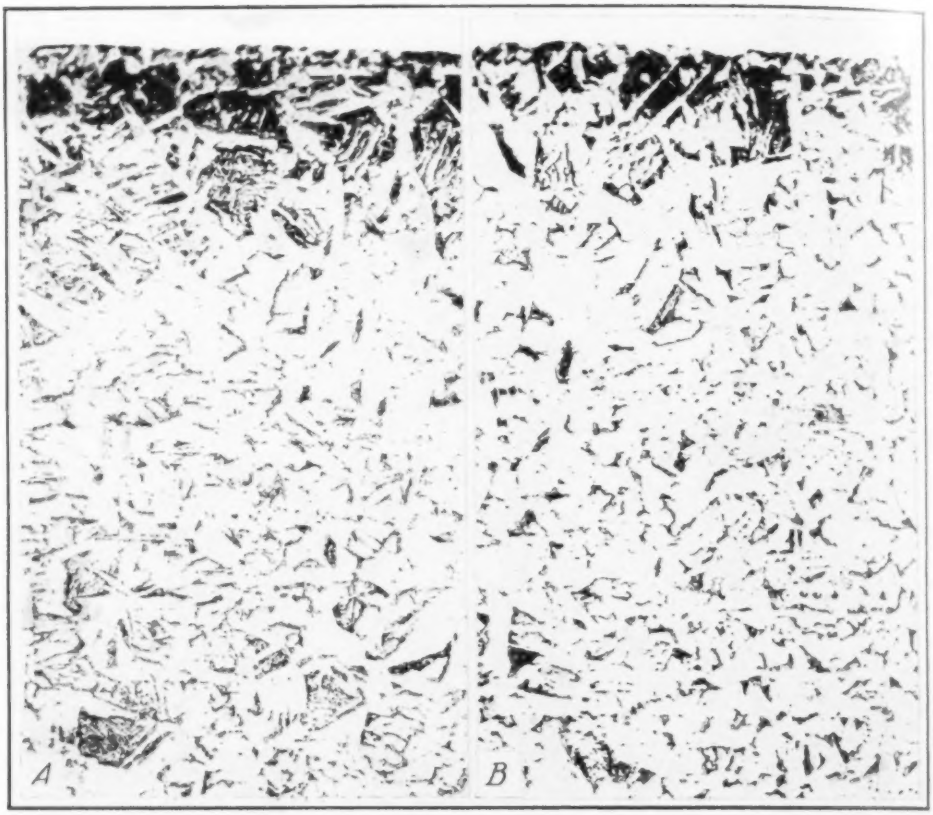

Fig. 8—Rapid Surface Recarburization in Butane-dissociated Ammonia Atmosphere Containing Water Vapor. The Sheets were also Normalized and Bright Annealed by this Treatment.

A. Maintained 3 Minutes at 960 Degrees Cent. (1760 Degrees Fahr.) in Dissociated Ammonia Containing 2 Per Cent Butane and Water Vapor. × 200.

B. Maintained 3 Minutes at 950 Degrees Cent. (1740 Degrees Fahr.) in Dissociated Ammonia Containing 3.25 Per Cent Butane and Water Vapor. × 200.

finished products such as razor blades, files and saws. The decarburization is usually due to surface oxidation during hot rolling where the iron oxide reduces the cementite, the carbon being eliminated as carbon monoxide. Another cause arises from the presence of surface defects in the steel; oxidized seams or oxide inclusions near the surface.

Examples of the latter defect taken from file blanks can be observed in the accompanying illustrations, Fig. 9.

Surface recarburization of these materials has been effected in butane-dissociated ammonia mixtures in batch anneal type furnaces using about 1 per cent butane during the course of a conventional spheroidizing or softening treatment. Limited but definite sooting of the steels was observed during these tests.

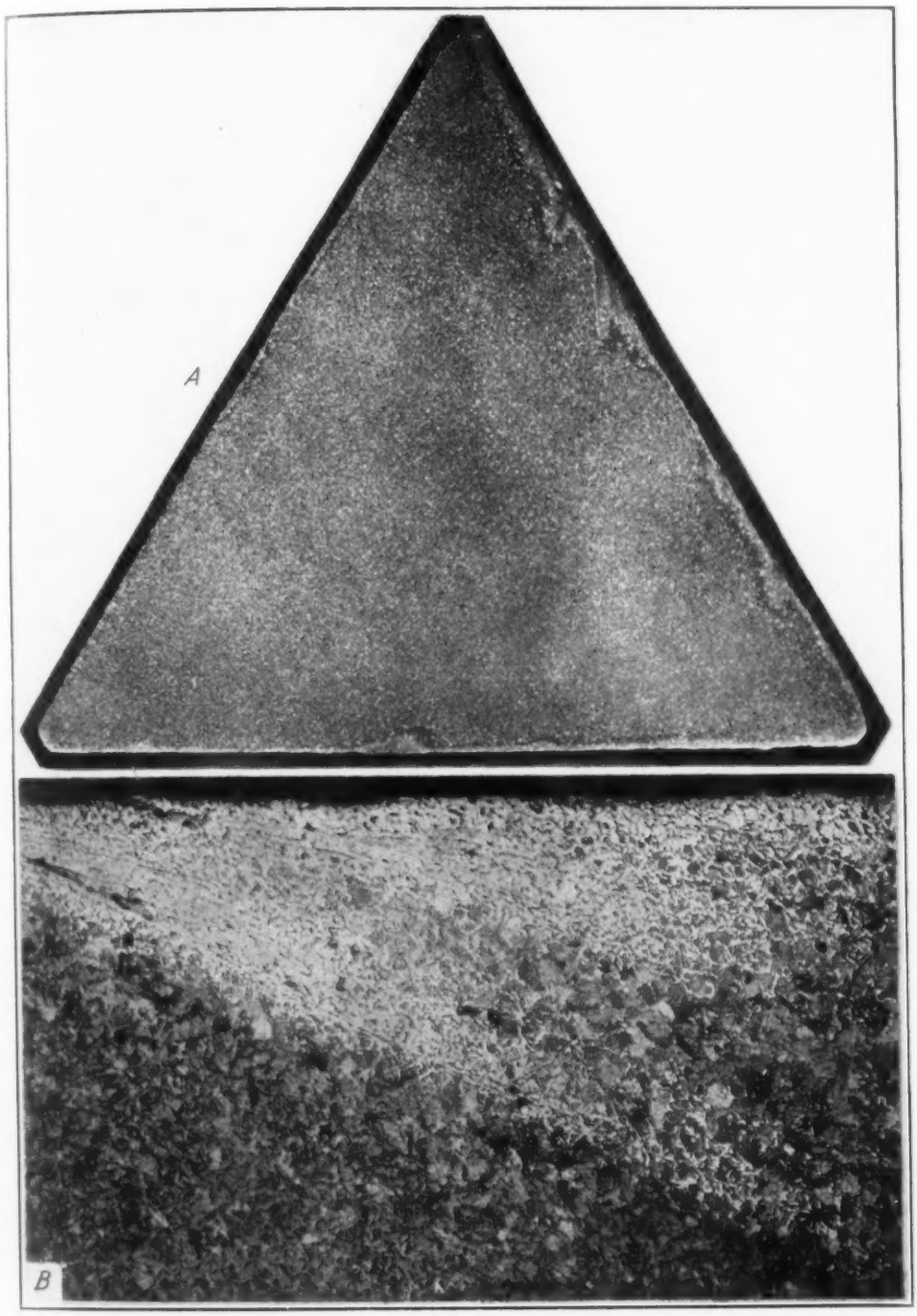

Fig. 9—Examples of Surface Decarburization Found in File Blanks Prior to a Softening Anneal.

A. Macrophotograph of Section Through 3-Cornered File Blank Polished and Etched. × 10.

B. Microsection Taken From Sample Indicating Pronounced Surface Decarburization Due to Presence of Oxide Inclusions. × 100.

It may be reiterated that the maximum carbon content which can be put back into the surface of the steel depends wholly on the maximum temperature of annealing (assuming an atmosphere saturated with respect to carbon). Thus it is necessary to attain a temperature indicated by the Acm line for the steel in question if the carbon content of the surface is to be raised to a concentration equal to that of the core. In spheroidizing, the temperature is maintained below Acm, and hence the full carbon content cannot be returned by carburization, for carbon transfer ceases as soon as the concentration is equal to that indicated as equilibrium at the maximum temperature used.

It is uncertain how important is this lack of extra hypereutectoid carbon in the surface as regards the physical properties or hardness of the surface.

The character of the surface of the steel to be annealed appears also to have a definite influence on the reactions taking place at the gas-metal interface. It seems well established that marked deposition of soot interferes with the rate of carburization. Jominy[10] states that "the carbon black that is precipitated is quite inactive, and tests have shown that it will not carburize a plain carbon steel in one hour's exposure, until temperatures higher than 1260 degrees Cent. (2300 degrees Fahr.) are reached." The same writer also makes reference to the effect of scale on decarburization.

The present writer's observations confirm the assertion that the presence of an oxide film on the steel can have a definite effect on carburization and decarburization. Thus it is frequently found that the treatment of an oxidized surface resulted in an increase or decrease in the peripheral carbon content of the steel even when no change could be discerned by microscopic examination of the peripheral parts of machined, oxide-free surfaces of the same pieces of steel. To summarize, there is reason to believe that preoxidation of the surface of steel greatly facilitates subsequent carburization or decarburization of that surface when the gas concentrations are altered but slightly from those required to prevent any interchange of carbon at the gas-metal interface. The problem is complicated, and with our present limited knowledge it is unwise to be dogmatic on the matter.

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[10]W. E. Jominy, "The Surface Decarburization of Steel at Heat Treating Temperatures", University of Michigan Engineering Research Bulletin, No. 18.

3. *High Carbon Steel Annealed in Pure Dry Hydrogen*

The commercial anneal of high carbon steels in pure dry hydrogen appears to merit consideration. For many years there appears to have been a divergence of opinion on the relative decarburizing power of pure hydrogen and hydrogen containing water vapor. Recent published work[11] by the writer has provided specific data on the role of water vapor on the surface decarburization of steels in a hydrogen atmosphere, at 800 degrees Cent. (1470 degrees Fahr.). This temperature was selected as approximating that used in the spheroidizing anneal of high carbon steels.

It was demonstrated that the "pure gas" has a definite but extremely limited decarburizing power on hypereutectoid steels, and that as the water vapor content of the moist hydrogen gas is increased (except in very low concentration) the decarburizing power is also profoundly increased. In very low concentration (10 milligrams water vapor per cubic foot hydrogen) the presence of the water vapor appears to reduce further the limited decarburizing power of the dry gas.

Metallographically this effect is clearly demonstrated in the accompanying two sets of microstructures of the surface of a plain carbon and a 1.5 per cent chromium steel subjected to the atmosphere indicated at 800 or 750 degrees Cent. for 55 hours. (Figs. 10 and 11.)

Some commercial tests following the above fundamental research are illuminating. The tests were conducted on high carbon steel rod using dried dissociated ammonia as the most convenient source of "pure hydrogen" (hydrogen free from water vapor or other oxygen bearing gas). The cracking unit was described by Berliner more than two years ago in *Metal Progress*. It is essential that the dissociating unit is maintained in good condition so that free ammonia is not liable to pass over into the annealing chamber with the consequent possibility of nitriding.

The general arrangement of the charge in the form of ½-inch coiled wire is illustrated in Fig. 12. The distribution of several ground cylinders may also be observed.

Under proper running conditions dissociated ammonia is practically free from moisture, but a conditioned activated-alumina tower was added to ensure low moisture content. This permitted the gas

[11] loc. cit.

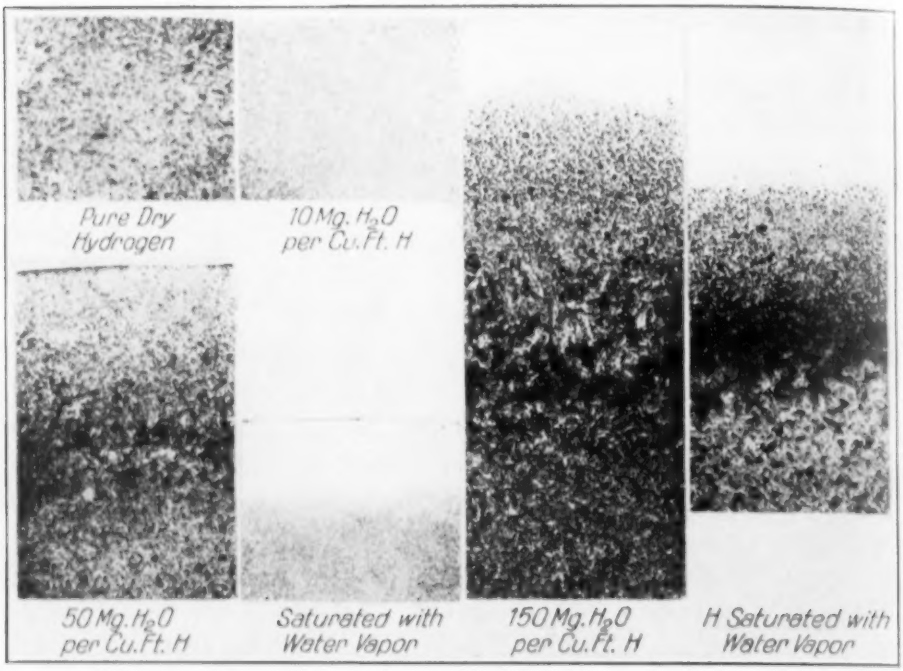
Pure Dry Hydrogen
10 Mg. H_2O per Cu. Ft. H
50 Mg. H_2O per Cu. Ft. H
Saturated with Water Vapor
150 Mg. H_2O per Cu. Ft. H
H Saturated with Water Vapor

Fig. 10—Photomicrographs Illustrating the Role of Water Vapor in the Decarburization of Plain-Carbon Steel by Hydrogen. Carbon 1.11 Per Cent and Manganese 0.29 Per Cent. Held 55 Hours at 800 Degrees Cent. (1470 Degrees Fahr.). × 100.

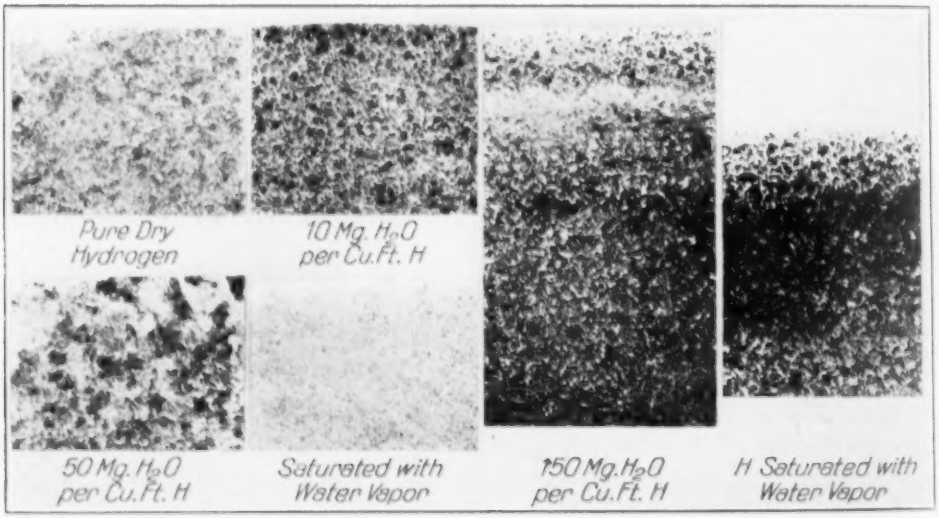
Pure Dry Hydrogen
10 Mg. H_2O per Cu. Ft. H
50 Mg. H_2O per Cu. Ft. H
Saturated with Water Vapor
150 Mg. H_2O per Cu. Ft. H
H Saturated with Water Vapor

Fig. 11—Photomicrographs Illustrating the Role of Water Vapor on the Decarburization of Chromium Steel by Hydrogen. S.A.E. 52100 Steel. Carbon 1.07 Per Cent, Manganese 0.31 Per Cent, Chromium 1.42 Per Cent. Held 55 Hours at 800 Degrees Cent. (1470 Degrees Fahr.).

to be dried so that a dew point of —60 degrees Fahr. (about 1 milligram of water per cubic foot) can readily be obtained.

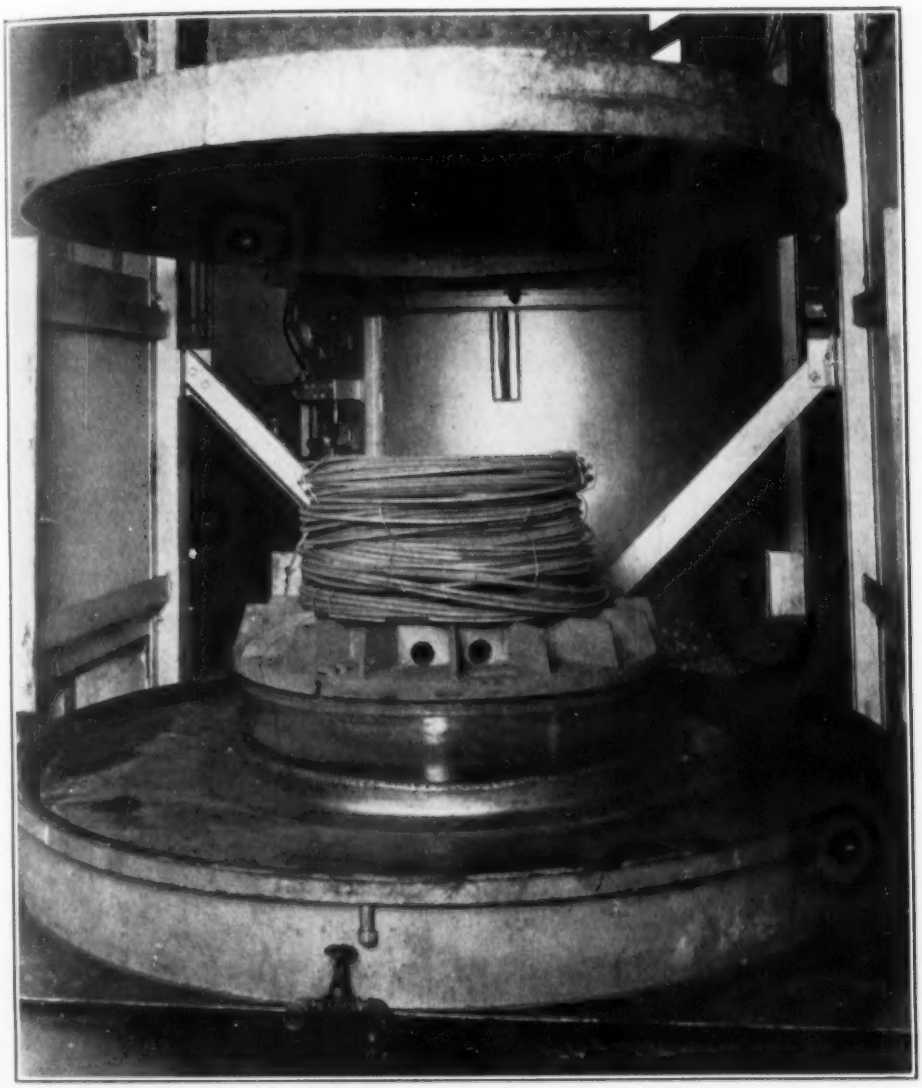

Fig. 12—Commercial Spheroidizing Anneal of High Carbon Steel Wire in Dried Dissociated Ammonia Whereby Surface Decarburization is Prevented.

Two test runs were made. In the first the coil consisted of carbon drill rod stock in the hot-rolled pickled condition. Pieces of drill rod and Berkshire rod, ground free from any surface decarburization, were also distributed throughout the charge. The drill rod contained about 0.1 per cent chromium and nickel, and the Berkshire rod about 1/3 per cent chromium and 1¼ per cent tungsten. Both steels contained about 1.2 per cent carbon. The charge was held two hours at a maximum temperature of 775 degrees Cent. (1430 degrees Fahr.).

During the course of the test it was noted (by dew point de-

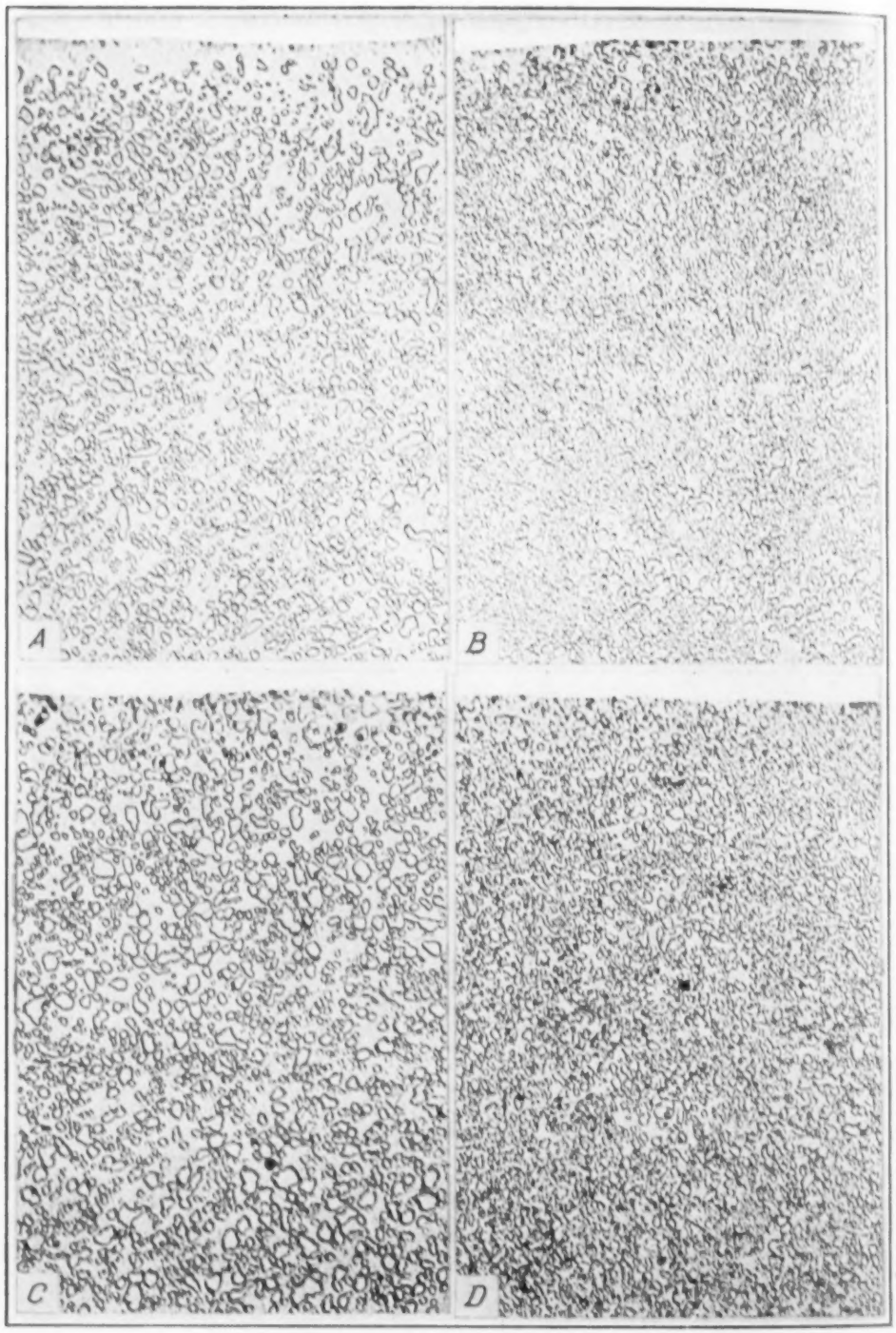

Fig. 13A and B—Surface Decarburization Occurring When the Spheroidizing Anneal Takes Place in Hydrogen (Dissociated Ammonia) Containing Appreciable Amounts of Water Vapor.

A. Carbon Steel Drill Rod Annealed in Dissociated Ammonia Atmosphere. × 500.

B. Berkshire Drill Rod Annealed in Dissociated Ammonia Atmosphere. × 500.

Fig. 13 C and D—Efficient Spheroidizing Anneal in Dry Dissociated Ammonia. No Surface Decarburization can be Detected.

C. Carbon Drill Rod. × 500.

D. Berkshire Drill Rod. × 500.

termination of effluent gas) that the moisture content approximated 70 milligrams of water vapor per cubic foot. It was considered that this was due to the reduction of the surface film of oxide on the coils left by insufficient pickling. Decarburization was to be expected. Chemical and metallographic analysis confirmed this. The photomicrographs show slight decarburization in both sets of ground samples. No chemical data is given. Fig. 13 A and B.

In the second test coils of Berkshire drill rod steel care was exercised that the hot-rolled coils were pickled free from scale so that there was little oxide present in the charge to permit the formation of water vapor in any appreciable quantity. A similar annealing cycle was used. Test on the effluent gas indicated much greater success in keeping the moisture content down to 10 milligrams per cubic foot.

The results of both chemical and metallographic analyses on this second test are presented for examination.

Table II

Carbon Tests on Ground Pieces (Second Test Run)

Carbon Drill Rod

0.600 Inches Round

Surface carbon of samples as submitted was 1.21 per cent. Surface cuts of 0.010 inches were made after annealing.

	Carbon Analysis After Anneal				
Specimen No.	1	2	3	4	5
1st cut	1.21%	1.20%	1.21%	1.17%	1.20%
2nd cut	1.21%	1.25%	1.22%	1.22%	1.20%

Berkshire Drill Rod

0.670 Inches Round

Surface carbon of samples as submitted was 1.21 per cent.

	Carbon Analysis After Anneal				
Specimen No.	1	2	3	4	5
1st cut	1.20%	1.21%	1.22%	1.18%	1.22%
2nd cut	1.20%	1.20%	1.20%	1.18%	1.22%

Table II gives the chemical data on the ground rounds which were known to be free from decarburization before annealing. It will be noted that surface decarburization was still absent after the anneal. Photomicrographs of a sample from each steel confirms this observation. Fig. 13 C and D.

Table III

Carbon Tests on Rolled Steel Coils (Second Test Run)
Berkshire Drill Rod—Carbon Tests

Coil. No.	Step of 0.010" on Diam.	On Outside End Before Annealing	On Outside End After Annealing	On Inside End Before Annealing	On Inside End After Annealing
1	1st cut	0.98	0.02	1.05	1.08
	2nd cut	1.05	1.08	1.08	1.10
	3rd cut	1.11	1.14	1.13	1.16
	4th cut	1.17	1.18	1.20	1.17
2	1st cut	1.01	1.05	1.05	1.10
	2nd cut	1.08	1.09	1.10	1.12
	3rd cut	1.13	1.14	1.16	1.13
	4th cut	1.16	1.15	1.20	1.15
3	1st cut	1.03	1.11	1.05	1.10
	2nd cut	1.08	1.12	1.11	1.13
	3rd cut	1.18	1.07	1.18	1.14
	4th cut	1.25	1.19	1.20	1.19
4	1st cut	1.10	1.10	1.01	1.10
	2nd cut	1.11	1.12	1.10	1.10
	3rd cut	1.15	1.14	1.12	1.15
	4th cut	1.19	1.15	1.13	1.16
5	1st cut	1.02	1.06	1.02	1.07
	2nd cut	1.11	1.10	1.09	1.10
	3rd cut	1.14	1.13	1.16	1.15
	4th cut	1.16	1.15	1.19	1.16

The data in Table III also provides chemical analyses from different parts of the charge for the hot-rolled pickled Berkshire rod. It may be noted that the carbon concentration gradient is less after the anneal than before. This is due to diffusion of carbon from the interior.

DISCUSSION

R. J. COWAN:[1] The paper Dr. Austin has presented is valuable in that it brings to us a broad survey of the general subject of bright annealing. It deals specifically with bright annealing of steel, and refers to carburizing and other special heat treatments that are indeed very interesting. In this broad survey of the subject he mentions also the annealing of nonferrous metals and suggests a number of things that raise questions in my mind.

In the solution of problems of this kind, we pay great respect to the men who carry on the essential fundamental observations, but when we come to reduce these to practical operation, we find many things that are pretty difficult. The fine interest that is shown in this matter of heat treatment in controlled atmospheres is certainly very commendable at this time, but it seems to resolve itself into a problem of how to work the matter out. The interesting thing is that when we come to reducing these ideas to practice the little apparently insignificant things are of great importance. Dr. Austin has mentioned the bright annealing of brass and nonferrous metals. We naturally would think that the thing to do would be to pick out a gas composition from the books and reproduce that composition and everything would be set. Unfortunately, that

[1]Metallurgical engineer, Surface Combustion Co., Toledo, Ohio.

is only a starting point. While, as I have said, we must pay great respect to the men who have done the fundamental work, working these things out practically is many times extremely difficult and holds the key to the whole situation. So when we are considering this problem, it has to be considered not only from the standpoint of particular atmospheres employed, but how these atmospheres are to be employed. One illustration comes to mind in connection with the use of methanol for bright annealing brass in a flue gas atmosphere. There you would naturally think that the atmosphere requirement would be simple—only flue gas and menthanol. When we attempted to do this in practical shop operation, we found by using a heat resisting alloy muffle that the desired reaction took place on the walls of the muffle rather than on the metal we were interested in, and we had then to go back and work out something in connection with the alloy to enable us to get the desired results. This is only one illustration of the idea that I am speaking of, for in the bright annealing of all these different metals, referred to, there are little practical kinks—methods of introducing the gas—particular alloys used, and so on, that have as much to do with satisfactory operation as the particular atmosphere used. These considerations are fundamental to the operation of these processes. There will be many disappointments if more attention is not given to this phase of the matter.

A. B. KINZEL:[3] Recent work on bright annealing, both from laboratory and shop standpoint, leads to the conclusion that these equilibrium diagrams may not be directly applied to production work. This is not intended to imply that the equilibrium diagrams are in error, but rather that the conditions in bright annealing applications are so complex that they cannot be accurately postulated. This leads to the thesis that the gases to be used for bright annealing should be oxygen-free, and this includes freedom from compounds of oxygen as well as molecular oxygen. We also contend that due to the complexity of conditions, carbon compounds should be avoided in bright annealing work. One gas which we have successfully used is a mixture of hydrogen and nitrogen in proportions varying according to the case desired, but generally of the order of magnitude of 90 per cent nitrogen and 10 per cent hydrogen. Moreover, the gas is free of molecular oxygen, and the CO_2 is sufficiently low so that it cannot be detected with barium hydroxide. The question of moisture in such gases depends upon the rate of cooling of the work. If the rate of cooling is very slow, very small amounts of moisture may be quite damaging, and the gas should be dried to the order of magnitude of one-tenth of a grain of moisture per cubic foot.

The author mentions the fact that cracked ammonia results in decarburization in certain instances. For some types of work, this is not undesirable, but when material is subject to a deep drawing operation, decarburization increases the tendency to produce stretcher-strains and is therefore not permissible. Another factor involved is the etching effect of gases with high hydrogen concentration, and this must be given careful consideration. Unfortunately, it does not seem to correspond with any theoretical data available.

The author's implication that it might be well to anneal stainless steel with the object of obtaining a tarnished, although not scaled, surface is in-

[3]Metallurgical engineer, Union Carbide and Carbon Co., New York.

teresting. However, it is much more difficult to pickle such a surface than a more heavily oxidized one, so that the commercial aspect of such a process is not particularly encouraging.

About a year ago, it was indicated that decarburization by hydrogen would be at a minimum with an optimum moisture concentration, this optimum being appreciably above zero. We are wondering if Dr. Austin has any further data on this subject.

Author's Reply

I would like to begin by thanking the speakers for contributing to the discussion on this orally-presented paper. It is unfortunate that the paper was not submitted in time to permit preprinting as I have had time only to present some of the more important features of the subject.

Mr. Cowan naturally emphasizes some of the practical aspects of the work but when he has had the opportunity to review the paper I feel that he will agree that this phase of the subject has not been entirely neglected. I rather anticipated that Mr. Cowan would speak of annealing brass, and reference to his work has been made in the paper.

We have had considerable contact with the commercial side of this work and soon concluded that if it were going to be practicable to bright anneal brass under commercial conditions it might be well first to determine on an experimental basis what those conditions should be. Up to the present, with any work with which I have been associated, the 100 per cent bright anneal of brass, even on the so-called test-tube scale, has not been satisfactorily accomplished. I am aware that Mr. Cowan suggested some time ago in a publication that the introduction of methanol resulted in a satisfactory bright anneal but I believe Mr. Cowan now finds that on an industrial scale at least it is unsatisfactory.

There are many factors with reference to the gas atmosphere which come into the problem, and to comment generally, I suspect that the trend in bright annealing will be toward gas-tight furnaces and highly perfected gases when dealing with batch type anneal. On turning to continuous anneal we seem to have another problem because design, or lack of same, does not yet permit real gas economy and consequently an expensive gas is out of the question.

There are some points raised by Dr. Kinzel to which I should like to make reference. He appears to state that no carbon compound should be present on the bright anneal of steels. It should be stated an important phase of this work is the section which demonstrates that the introduction of certain concentrations of hydrocarbons into a reducing atmosphere leads to a desired controlled surface recarburization concomitant with true bright anneal.

With reference to the etching effect of hydrogen I do not believe that I have encountered this trouble so frequently as have other investigators. Thus in Fig. 1 the mirror-like surface of the annealed sheets is indicated by the perfect reflections observed.

In a previous paper, as Dr. Kinzel mentions, it was suggested that minimum decarburization was obtained with a slight but definite concentration of water vapor in hydrogen. This referred specifically to a temperature of 800 degrees Cent., and check runs were made to confirm the observation. No further data are available on this subject but it is hoped to conduct a similar experimental analysis at considerably higher temperatures.

OXIDATION OF A LOW CARBON STEEL IN THE TEMPERATURE RANGE 1650 TO 2100 DEGREES FAHR.

By Clarence A. Siebert and Clair Upthegrove

Abstract

A paper presented at the 14th annual convention of the American Society for Steel Treating by Upthegrove and Murphy (1) gave data on the scaling of S.A.E. 1020 steel in atmospheres of air, oxygen, steam, and carbon dioxide. They reported unexpected deviations in the temperature curves for both oxygen and air between 1800 and 2000 degrees Fahr., and pointed out that these deviations were accompanied by the formation of blisters on the surface of the steel. The present research was undertaken to further investigate these phenomena by a study of the effect of temperature, time, and partial pressure of oxygen in the scaling atmosphere in the temperature region 1650 to 2100 degrees Fahr.

Literature

PREVIOUS researches on the general subject of scaling have been reviewed in previous publications from this laboratory by Murphy, Wood and Jominy (2)* and Upthegrove and Murphy (3). A brief survey of those publications which have a direct bearing on this investigation will be given here.

A large number of empirical researches giving actual scaling data have been reported. For the most part the investigators have used gain in weight as the criterion of scaling, a condition which does not always permit ready comparisons with the data obtained in this investigation in that the scaling was determined as loss in weight. Other than from the standpoint of the differences in the criterion of scaling, practically none of these researches have a direct bearing on the present study, since the temperatures used do not cover both the zones of increasing and decreasing scaling effects

*The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Sixteenth Annual Convention of the Society held in New York City, October 1 to 5, 1934. Of the authors, Clarence A. Siebert is associated with the Metal Products Division, U. S. Rubber Co., Detroit, and Clair Upthegrove is Professor of Metallurgical Engineering, University of Michigan, Ann Arbor, Mich. Manuscript received June 20, 1934.

observed by Upthegrove and Murphy, or different atmospheres were used. Schroeder (4) using loss in weight as the measure of scaling reports an increase in scaling in combustion atmospheres on increasing the temperature from 1650 to 2190 degrees Fahr. (900 to 1200 degrees Cent.) as do Upthegrove and Murphy from 1500 to 1900 degrees Fahr. (815 to 1040 degrees Cent.). This, however, would be expected from the behavior of carbon dioxide and water vapor curves reported by Upthegrove and Murphy (5).

Heindlhofer and Larsen (6) derived an expression for the effect of time on scaling by means of differential equations and arrived at the conclusion that the oxidation was proportional to the square root of the time. They assumed a constancy of membrane structure which was not confirmed in the present investigation. They, however, investigated scaling over comparatively long periods of time. Their experimental data at 1020, 1110, 1830, 2010 degrees Fahr. (550, 600, 1000 and 1100 degrees Cent.) deviated considerably from the theoretical equation. They postulated that the interface of the various layers was composed of the mixed phases, that is FeO + Fe_3O_4, or Fe_3O_4 + Fe_2O_3, and that the layers themselves were composed of the single solid solution beginning with Fe_2O_3 in the outer layer, Fe_3O_4 in the middle layer, and FeO in the inner layer. Their photomicrographs presented do not appear to offer confirmation of this statement.

Several theories have been advanced to account for the mechanism of oxidation. Pilling and Bedworth (7) suggested that the continued oxidation of a metallic surface occurred by reason of the diffusion of oxygen inward through the previously formed layers of scale. The scale had to expand outward because of the greater volume of the oxide compared with that of the metal. This necessarily assumes plastic properties for the scale, an assumption which, however, has been a point of serious objection.

Fedotjev and Petrenka (8) advanced the theory that the alternate formation and reduction of higher and lower oxides of iron were responsible for continued oxidation. In their mechanism they considered that FeO was formed first and then oxidized to Fe_3O_4. The Fe_3O_4 was then reduced by the iron in contact with it to FeO so that additional iron was oxidized in this process. The FeO was oxidized again to Fe_3O_4 and the process repeated.

Pfeil (9) proposed a mechanism involving a double diffusional process, that is, the diffusion of oxygen inward accompanied by an

outward diffusion of some form of iron. This does not require the scale to have extreme plastic properties. In his investigations he has shown that scales of different iron contents can react with one another, that is when two samples of scale whose average iron contents were in excess of 72 per cent were heated in a vacuum or in purified nitrogen, an exchange of oxygen occurred until both samples had the same analysis. Likewise when a large amount of oxygen-rich scale was used so that the average iron content was less than 72 per cent, the iron-rich scale decreased in iron content to 72 per cent when the reaction stopped. Raising the temperature had no effect on changing the compositions of the two scales.

Method

The method used in this investigation was essentially the same as used by Upthegrove and Murphy (10). The samples were heated in an electric furnace of the Globar type which contained a glazed porcelain tube 40 inches long and approximately two inches in diameter. One end of the tube was sealed with a two-hole refractory stopper through which the gas inlet tube and thermocouple protection tube was led. In order to avoid scaling during the introduction of the sample into the furnace or during the time required for stabilizing the furnace temperature, the furnace was first thoroughly flushed with purified nitrogen. The flow of nitrogen was then continued while the sample was being introduced and the furnace brought to the predetermined temperature. The nitrogen was then cut off and the scaling agent turned on. At the end of the scaling period the oxidizing agent was cut off and the flow of purified nitrogen again turned on. The sample was immediately withdrawn and quenched in distilled water. The sample was suspended in a chromel wire boat during the run and was placed so that it was centered in the furnace one quarter of an inch below the thermocouple bead.

The atmospheres used in the studies were mixtures of oxygen and nitrogen in varying ratios. The total volume of the gas was such that a linear velocity of thirty feet per minute was maintained. The atmospheres were obtained by adding oxygen or nitrogen to dry air, depending upon whether greater or smaller percentages of oxygen than that in the air were desired. All gases were carefully purified by passing them through trains consisting of calcium chloride, ascarite, and dehydrite tubes to affect removal of CO_2 and water

vapor. The flow was measured by means of flow meters of the friction type which were calibrated against a Sargent wet test meter. Gas analysis was used as a check on the computed percentages from the flow meter readings.

While the greater part of the scale always split off in the quenching operation, the small amount adhering was removed in an electrolytic stripping bath. The sample was then washed, dried, and weighed. The loss in weight was expressed in terms of pounds per 100 square inches of original surface. The scale that split off was filtered, dried, and analysed for ferrous and total iron.

The samples used were 2½ inches long and ⅝ inch in diameter, after machining and polishing through 00 emery paper. The analysis of the steel used was:

Carbon	0.20 Per Cent
Manganese	0.45
Silicon	0.17
Sulphur	0.030
Phosphorus	0.017

Results

The scope of this investigation was limited to the influence of temperature, time, and partial pressure of oxygen in the oxidizing gas. The effect of the variation of gas velocity was not studied, for increasing the flow above five feet per minute does not affect the scaling loss.

Effect of Variation of Temperature

The data which were obtained when the temperature of exposure was varied from 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.), using air and oxygen as the scaling media, are summarized in Fig. 1. Both curves show regions where the amount of scaling is actually lowered by increasing the temperature, the effect being more pronounced when air is used as the oxidizing medium than when oxygen is used. In air the scaling loss reaches a maximum at 1850 degrees Fahr. (1010 degrees Cent.) and a minimum at 2000 degrees Fahr. (1095 degrees Cent.), while in oxygen a maximum is reached at 1900 degrees Fahr. (1040 degrees Cent.) and a minimum at 1950 degrees Fahr. (1065 degrees Cent.). The chemical composition of the scales formed shows a similar trend in ferrous iron content. This is indicated in Fig. 2, where ferrous iron is plotted against temperature. A maximum ferrous iron content occurs

at 1775 degrees Fahr. (970 degrees Cent.) and minimum at 2000 degrees Fahr. (1095 degrees Cent.) when air is the oxidizing agent. For the scale formed in oxygen, maxima occur at 1800 and 1975

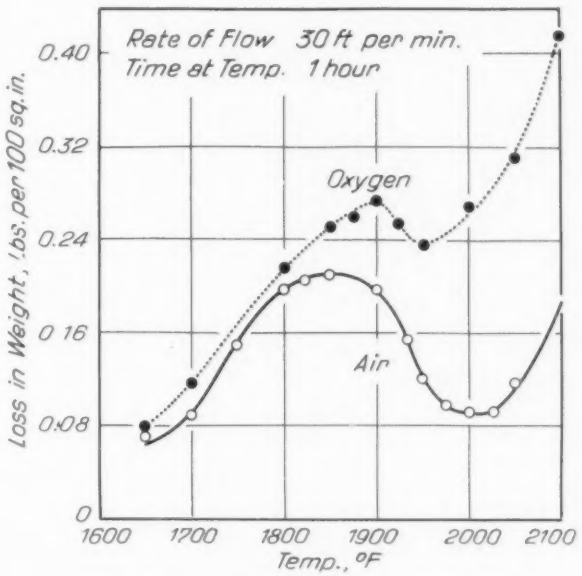

Fig. 1—Effect of Variation of Temperature on the Scaling of S.A.E. 1020 Steel.

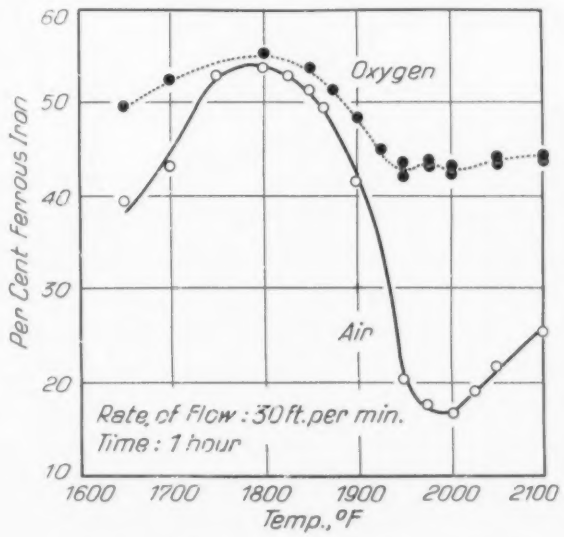

Fig. 2—Effect of Variation of Temperature on the Composition of the Scale.

degrees Fahr. (980 and 1080 degrees Cent.) and minima at 1950 and 2000 degrees Fahr. (1065 and 1095 degrees Cent.).

These data obtained by Upthegrove and Murphy (11) are sum-

marized in Fig. 3. A comparison of their results with those obtained in the present investigation shows certain differences to exist. They found in 2-hour scaling periods that the maximum scaling loss in air was reached rather abruptly at 1800 degrees Fahr. (980 degrees Cent.) and had fallen off considerably at 1900 degrees Fahr.

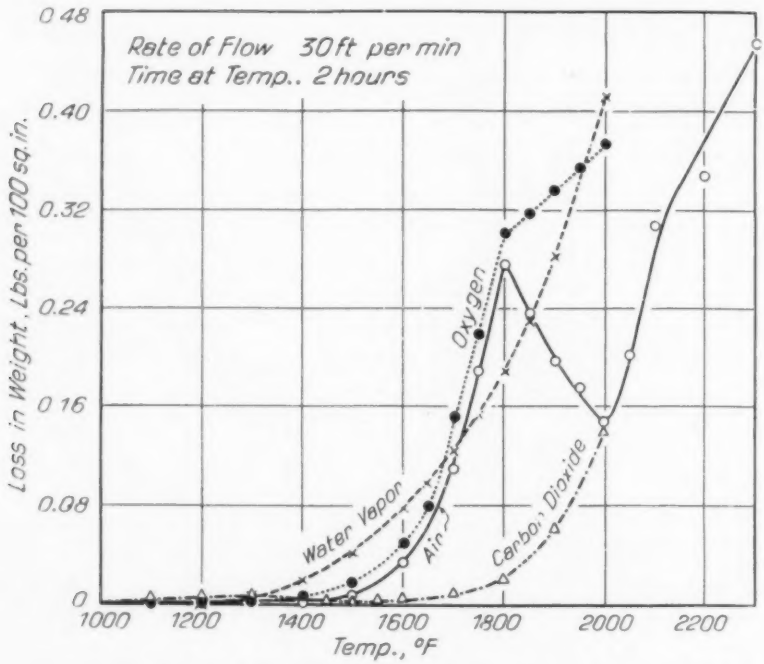

Fig. 3—Effect of Variation of Temperature on Scaling of S.A.E. 1015 Steel.

(1040 degrees Cent.). The present investigation, using a 1-hour period, shows the maximum to occur at 1850 degrees Fahr. (1010 degrees Cent.), with equal losses in weight at 1800 and 1900 degrees Fahr. (980 and 1040 degrees Cent.). Their work showed a retardation in oxygen at 1800 degrees Fahr. (980 degrees Cent.) while the present work not only shows a retardation at 1800 degrees Fahr. (980 degrees Cent.) or slightly above, but actually has a reversal at 1900 degrees Fahr. (1040 degrees Cent.). While at first it might appear that the differences were due to the use of different periods of scaling, the results of 2-hour tests in the present investigation, as shown in Fig. 4, clearly indicate this not to be the case. Chemical compositions of the steel do not offer an explanation in that the two are for all practical purposes identical.

	C	Si	Mn	P	S	H_2	O_2	N_2
U–M	0.18–0.20	0.17–0.22	0.45–0.48	0.021	0.03	0.00004	0.005	0.005
S–U	0.20	0.17	0.45	0.017	0.03	0.00002	0.004	0.004

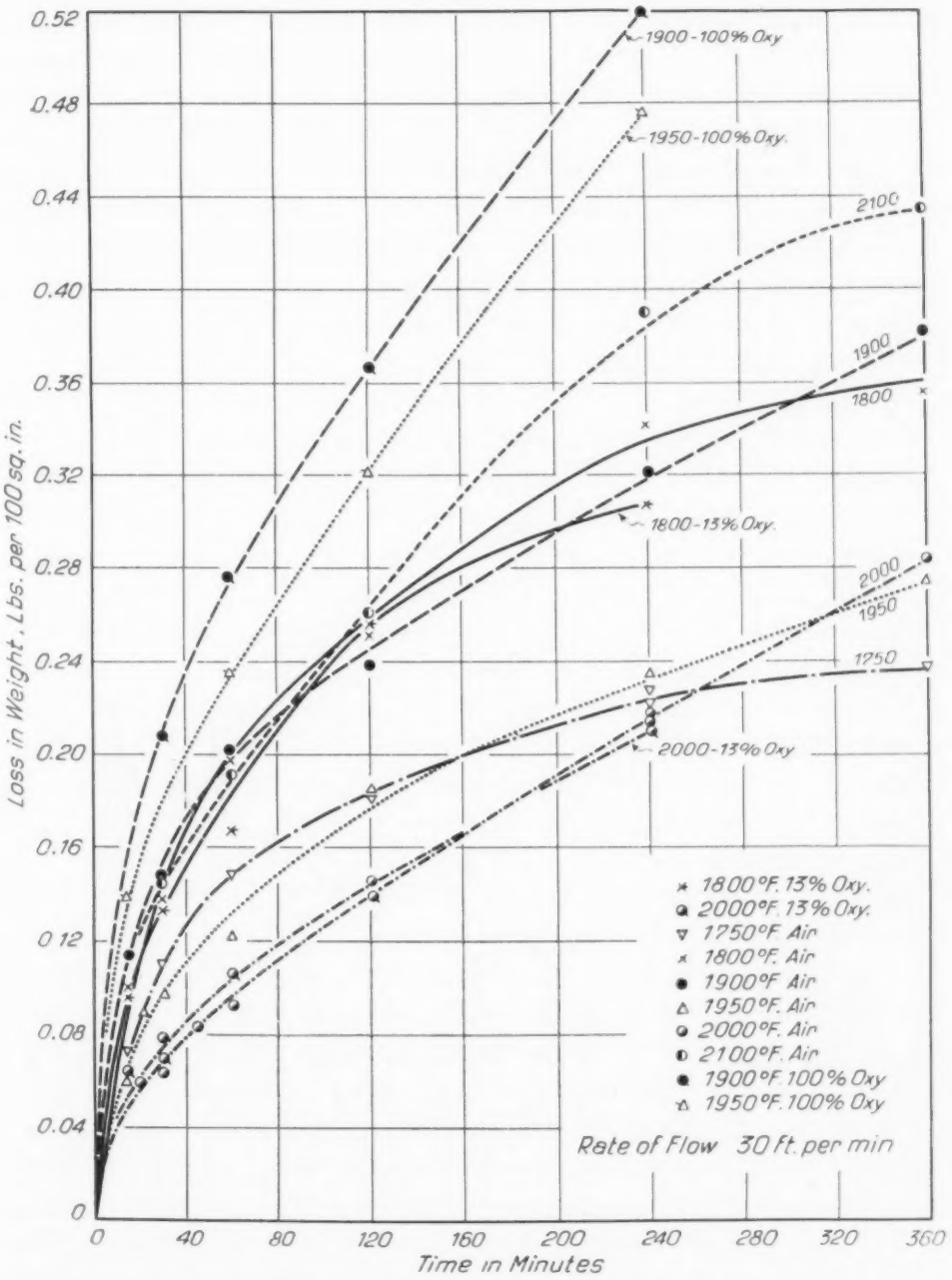

Fig. 4—Effect of Variation of Time on the Scaling Loss of S.A.E. 1020 Steel.

A difference, however, does exist in the method of production of the two steels. While both are open-hearth heats, the second was rolled from a small size ingot. It is known that differences in ingot size produce differences in physical properties and while this seems hardly probable it is possible that this may be a factor in the devia-

tions observed. The failure of Upthegrove and Murphy to report a reduction in scaling with increasing temperature in the oxygen atmosphere is more likely due to the fact that they used 50-degree temperature intervals rather than 25 degrees and as a consequence failed to observe definite indications of its occurrence. Their 1850 degrees Fahr. (1010 degrees Cent.) point actually fell slightly below the line joining the 1800 and 1850 degrees Fahr. (980 and 1010 degrees Cent.) points, but it was not looked on as significant at that time. As this stock was completely used up in the earlier investigation it was not possible to check this point.

Upthegrove and Murphy pointed out that the sudden change in the curves at 1800 degrees Fahr. (980 degrees Cent.) was accompanied by the formation of blister on the surface of the steel. They concluded that the blisters were areas where a higher degree of oxidation had occurred and due to the differences in specific volume of the different oxides of iron these blistered regions had buckled away, thereby interrupting the diffusional nature of the scaling process at these places. They believed that in time, contact would again be made, but in the meantime, the surrounding areas would have scaled to a greater extent, thereby creating the base relief pattern of the blisters. This will again be considered along with the authors' idea of the mechanism of this phenomenon.

Effect of Variation in Time

The effect of increasing periods of time on the oxidation of steel has been previously shown to produce data which when plotted result in curves of the parabolic type due to the diffusional nature of the scaling process. In the temperature range where blistering occurs it would then be expected that the data would plot as a broken curve if a mechanical interruption of the diffusional process occurred. If no mechanical effect existed a smooth curve of the parabolic type would be expected.

To determine whether or not such deviations would occur, time curves were obtained for oxygen, air, and 13 per cent oxygen at temperatures where scaling continued to increase with increasing temperatures and at temperatures where a decrease in scaling occurred with increasing temperatures. The effect of increasing periods of time on the scaling under these conditions is summarized in Fig. 4. In all cases, the effect of increasing time has been to decrease the rate of scaling and all curves are of the parabolic type.

The results obtained in oxygen at 1900 and 1950 degrees Fahr. (1040 and 1065 degrees Cent.) for periods of time up to four hours show that within the limit of time used there is no tendency for the rates of scaling to approach each other. Instead the decrease in the amount of scaling actually increases with increasing time. The increase in scaling losses in oxygen over those occurring in air also become greater at these temperatures as the time of contact is increased.

The study of the effect of time on the oxidation in air was carried out to six hours. Up to periods of four hours the curves rise rather rapidly with increasing time. Between four and six hours, however, the curves for 1750 and 1800 degrees Fahr. (955 and 980 degrees Cent.) tend to level off, while the curves for higher temperatures continue to rise at a practically unchanged rate with increasing time. A comparison of the scaling losses at the end of six hours with those at the end of one hour (Fig. 1) shows some changes in the form of the reversal. At the end of one hour at 1800 and 1900 degrees Fahr. (980 and 1040 degrees Cent.) equal losses in weight occur, and at 1950 degrees Fahr. (1065 degrees Cent.) a higher loss is found than at 2000 degrees Fahr. (1095 degrees Cent.). At the end of six hours, however, the loss at 1900 degrees Fahr. (1040 degrees Cent.) is slightly greater than at 1800 degrees Fahr. (980 degrees Cent.), and at 2000 degrees Fahr. (1095 degrees Cent.) exceeds that at 1950 degrees Fahr. (1065 degrees Cent.). Scaling loss at the end of one hour at 1800 degrees Fahr. (980 degrees Cent.) is greater than at 2100 degrees Fahr. (1150 degrees Cent.). The retardation effect with increasing time is greater at 1800 than at 2100 degrees Fahr. (980-1150 degrees Cent.) with the result that at the end of two hours the scaling is slightly greater at the upper temperature. This result is in agreement with the two-hour runs of Upthegrove and Murphy. Further increase of time up to six hours produces similar results with the rate of scaling at 2100 degrees Fahr. (1150 degrees Cent.) continuing to increase over that at 1800 degrees Fahr. (980 degrees Cent.).

The results obtained by scaling in an atmosphere containing 13 per cent oxygen at 1800 and 2000 degrees Fahr. (980 and 1095 degrees Cent.) show that the rates of scaling for periods up to two hours are slightly greater than in air at these temperatures. As the time is increased the retardation effect becomes more pronounced for the 13 per cent oxygen than for air, and the rate of scaling at

both 1800 and 2000 degrees Fahr. (980 and 1095 degrees Cent.) falls below that for air.

In interpreting the results of the time studies the question of whether or not the data point to the elimination of the reversal in the scaling or to its continuance with increasing periods of time occurs. While some of the above results seem to point very definitely

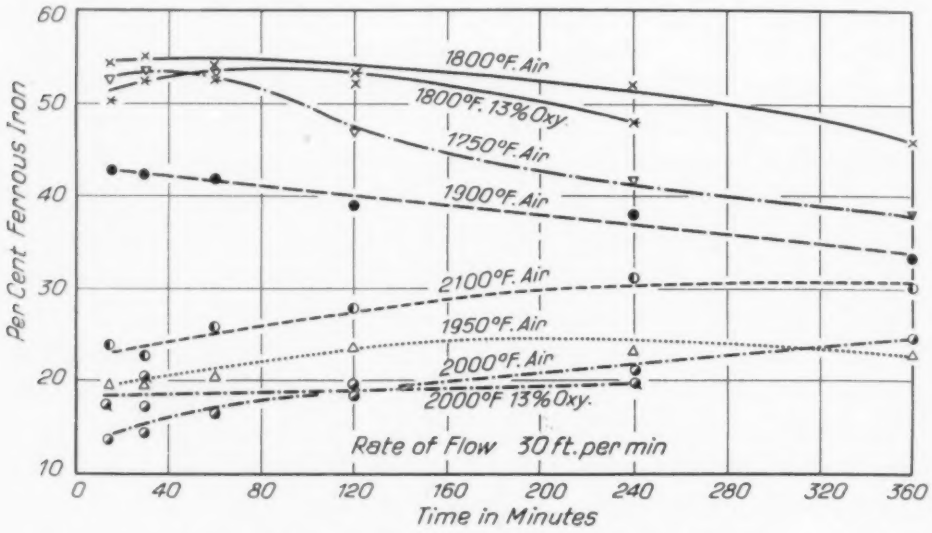

Fig. 5—Effect of Time on the Composition of the Scale.

to a smoothing out of the temperature effects, others indicate very definitely that this cannot happen unless the time is extended well beyond any of the heating periods employed in practice and possibly not then.

The scale analyses on the time runs are summarized in Fig. 5, where ferrous iron is plotted against time. For temperatures below 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content decreases with increasing time, and above 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content increases with increasing time. At 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content reaches a maximum at three hours.

A study of the surface of the scaled samples appears to offer a partial explanation for these effects. Specimens that were scaled for different periods of time in air at 1950 degrees Fahr. (1065 degrees Cent.) are shown in Fig. 6. The roughening of the surface, which is related to the occurrence of blistering, makes its appearance almost instantly, in fact is unmistakable on samples subjected to the scaling medium for only five minutes. This roughening which is very ap-

parent in the 15 minute samples of Fig. 6 increases with increasing time and at the end of six hours the entire surface has been affected. The progressive effect with increasing time is found at all of the temperatures studied, and can account for the falling off in the ferrous iron content with increasing time at 1750, 1800 and 1900 degrees Fahr. (955, 980 and 1040 degrees Cent.), as the blistering

Fig. 6—Roughening of Surface of Sample Scaled in Air at 1950 Degrees Fahr. for Periods of Time Varying from 15 Minutes to 6 Hours.

is accompanied by the higher degree of oxidation. It does not explain, however, the rise in ferrous iron content with increasing time at 2000 and 2100 degrees Fahr. (1095 and 1150 degrees Cent.). The possibility that at these upper temperatures all layers of the scale do not grow proportionately appears to offer a feasible explanation. If it can be assumed that the inside layer grew faster than the outer layers, then the ferrous iron content of the scale would increase with increasing time. While not enough data are available to draw any definite conclusions in regard to this point, the suggestion of nonproportional growth of the different layers is not believed to be incompatible with observed facts.

Effect of Variation of Partial Pressure of Oxygen

The atmospheres for this phase of the investigation were obtained by adding carefully purified and dried oxygen or nitrogen to purified and dried air. The data obtained are summarized in Fig. 7. The curves divide themselves into two distinct groups; those which show a rapid rise in scaling with oxygen contents ranging from zero to approximately that of air, with a slight but gradual increase from

that point out to 100 per cent oxygen; and those which show a rapid rise in scaling at very low oxygen contents, and then a more gradual but greater increase from that point to 100 per cent oxygen.

The temperatures that produce curves falling in the first group are 1650 through 1900 degrees Fahr. (900 through 1040 degrees Cent.). Those producing curves falling in the second group are

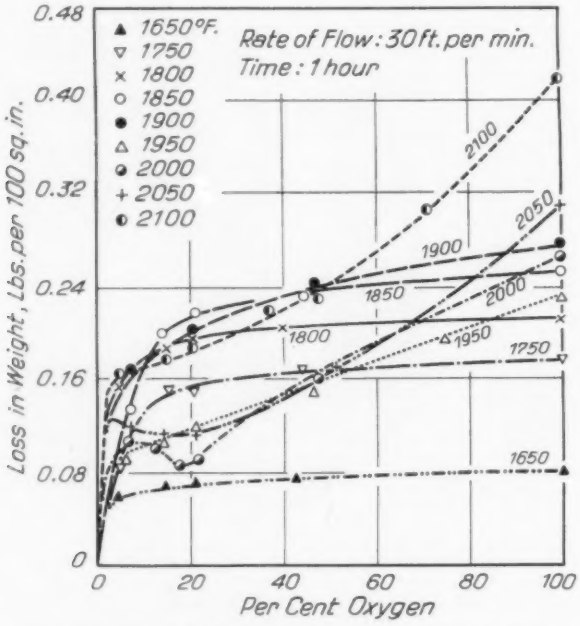

Fig. 7—Effect of Variation of Partial Pressure of Oxygen on the Scaling of S.A.E. 1020 Steel.

1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.). Two other definite characteristics are evident in the graphs of the second group. The curvature of the 2050 and 2100 degrees Fahr. (1120 and 1150 degrees Cent.) curves is concave upward while all of the others have curvatures that are concave downward, with the exception of the 1950 degrees Fahr. (1065 degrees Cent.) curve which is a straight line between 4 and 100 per cent oxygen. The 2000 and 2050 degrees Fahr. (1095 and 1120 degrees Cent.) curves reach a maximum at 7 and 3 per cent oxygen respectively and minima at 18 per cent oxygen in both cases.

A comparison of the loss in weight values for the different temperatures and different oxygen concentrations with the chemical compositions of the scales formed, which are shown in Fig. 8, shows that the ferrous iron contents of the scales follow the same trend

as the loss in weight. The curves divide again into two groups; 1650 through 1900 degrees Fahr. (900 through 1040 degrees Cent.) and 1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.). For temperatures of 1650 through 1950 degrees Fahr. (900 through 1065 degrees Cent.) the ferrous iron contents of the scales formed are nearly constant for oxygen concentrations of 20 to 100

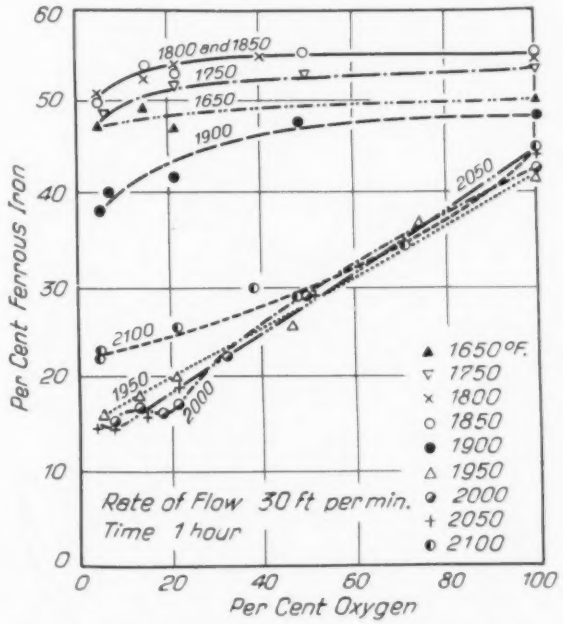

Fig. 8—Effect of Variation of Partial Pressure of Oxygen on the Composition of the Scale.

per cent. For temperatures of 1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.) a very definite and fairly uniform increase in ferrous iron occurs with increasing oxygen concentrations.

Attention is also called to the evidence in these curves of the possibility of retarded scaling effects with increasing temperatures without the occurrence of a higher degree of oxidation. The losses in weight in a 40 per cent oxygen atmosphere at temperatures of 1950, 2000 and 2050 degrees Fahr. (1065, 1095 and 1120 degrees Cent.) are found to be approximately equal. Reference to Fig. 7 shows that the ferrous iron contents of the three scales are approximately identical. This is a departure from the effect usually obtained where the retardation is accompanied by a change in the degree of oxidation. It is evident that not only the degree of oxidation, but also the way in which the ferrous and ferric iron and oxygen are

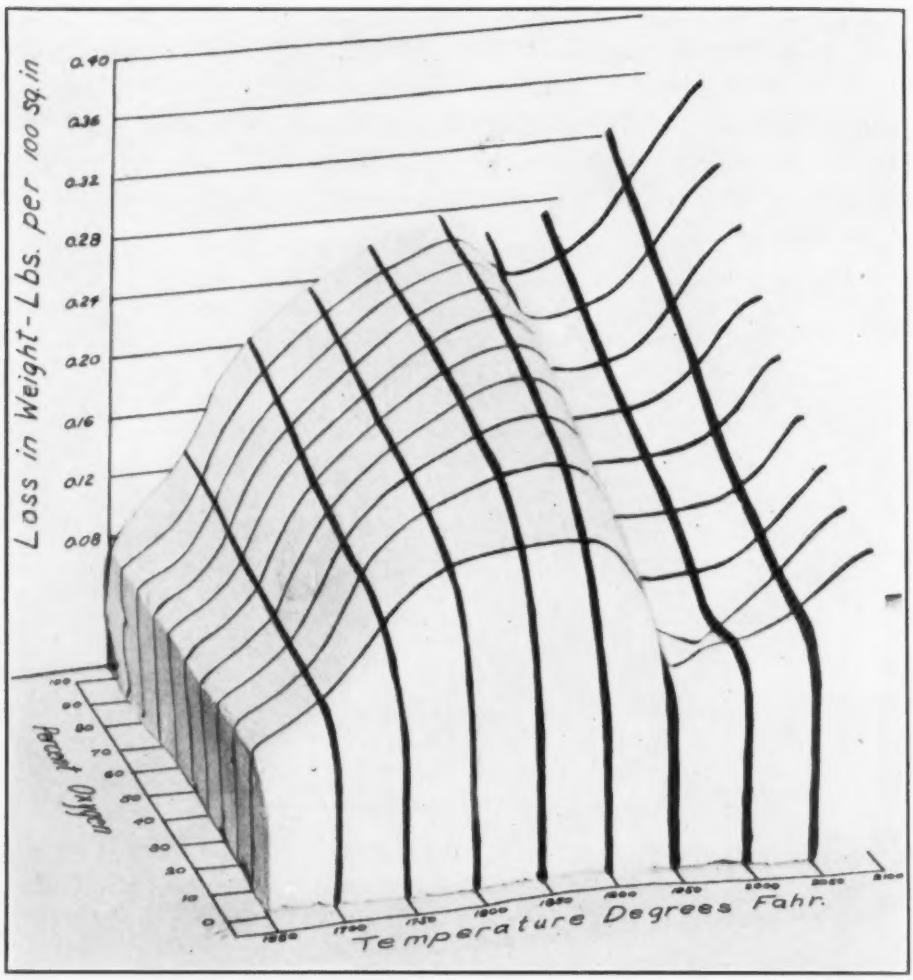

Fig. 9—Three-Dimensional Model Showing the Relationship Between Scaling, Temperature and Oxygen Content.

present in the solid solutions which are possible, must enter into the retarded scaling effects.

By constructing a three-dimensional model, a surface can be developed which shows the relationship between the scaling, the temperature, and the oxygen content of the oxidation atmosphere. Such a representation of the data is given in Fig. 9. The time of exposure was one hour in all cases. The reversal in the temperature curves at a constant partial pressure of oxygen is evident from very low oxygen contents to 100 per cent oxygen. The minimum in the curves broadens out at oxygen contents intermediate between air and 100 per cent, occurring over a range of approximately 100 degrees Fahr. at 40 per cent oxygen.

Mechanism

Before proceeding to the formulation of a possible mechanism to account for the decrease in scaling with increase in temperatures in the range 1850 and 2000 degrees Fahr. (1010 and 1095 degrees Cent.), the conclusions to be drawn directly from the data on effect of temperature, time, and partial pressure of oxygen will be briefly summarized.

A reversal, that is, a decrease in the amount of scaling with increasing temperature, occurs for all oxygen concentrations in the temperature range 1850 to 2000 degrees Fahr. (1010 to 1095 degrees Cent.).

The ferrous iron content of the scales formed undergoes a similar reversal, maxima and minima occurring under approximately the same conditions as for the occurrence of the maxima and minima in scaling.

The reversal or decrease in scaling with increasing temperature occurs for all periods of time up to six hours, the maximum time period used. For a 13 per cent oxygen atmosphere the extent of the reversal was increasing at the end of four hours.

The effect of increasing time on scaling in atmospheres of oxygen, air, and 13 per cent oxygen is in general the same regardless of whether or not the temperature is one at which the scaling is continuously increasing with increase in temperature or one at which the reverse conditions exist. The 100 per cent oxygen atmosphere shows the least retardation in scaling as time increases.

For those concentrations which show the greatest retardation in the rate of scaling with increase in time, the ferrous iron content of the scale is found to decrease. For those concentrations which show a less marked falling off in scaling the ferrous iron content of the scales is found to increase with time.

For certain oxygen concentrations the scaling losses and the ferrous iron content of the scales may remain practically constant over a given temperature range, or retardation of scaling with increasing temperatures may occur without change in the degree of oxidation.

Scaling a Diffusional Process

Upthegrove and Murphy pointed out that the sudden change in the slope of their temperature loss in weight curves for air and oxygen atmospheres was accompanied by the formation of blisters.

They suggested this change in the scaling was the result of a mechanical interruption of the process due to a breaking away of the scale at the blistered areas. This does not appear to adequately account for all of the results observed in the present investigation.

It is quite generally conceded that after the first film of scale is formed the continuation of the oxidation process is a diffusional phenomenon. The general equation for diffusion is

$$\frac{dW}{dt} = -D\,\frac{dc}{dx}$$

where dW is the amount of the substance under consideration which diffuses through a unit cross section in time dt under a concentration gradient of $\frac{dc}{dx}$, and D is a coefficient. From this it can be seen that the two factors controlling the scaling operation are the concentration gradient or driving force, and the coefficient of diffusion.

The study of the effect of time on scaling offers a means of determining the nature of the concentration gradient. Two types of curves may result in a time-scaling plot. It may be a straight line, that is, one in which the rate of scaling is constant, or a parabolic type, that is, one in which the rate of scaling decreases with time. The constant rate of scaling denotes a cellular membrane in which case the oxidizing gas diffuses mainly through the pores. Under such conditions the concentration gradient or driving force is the difference between the concentration of the oxidizing gas in the scaling atmosphere and at the metal-scale interfaces. The parabolic type indicates that the scale membrane is a continuous type and a continuation of the scaling process occurs by the solution of the oxidizing gas in the scale surface and then a diffusion of this gas inward. In this case the high potential side of the driving force is no longer the concentration of the oxidizing gas in the scaling atmosphere, but is the concentration of the gas in the surface of the scale itself. This will be considered again in the discussion of the diffusion through the various layers formed. The present studies gave time curves of the parabolic type.

As the solubility of the gases in metals generally increases with increasing temperatures, the surface in direct contact with the scaling atmosphere will be capable of taking up more oxygen at higher temperatures. This causes an increase in the concentration gradient or driving force. When differences in the degree of oxidation occur

at different temperatures, the solubility of oxygen may also change and its concentration in the scale may actually decrease when compared with the concentration at a lower temperature.

If it is assumed that the outer layer of the scale in all cases approaches a composition corresponding to Fe_2O_3, it would appear as if the degree of oxidation of the other layers was of no importance as far as the concentration gradient is concerned, as the overall gradient is governed by the difference in concentration of oxygen

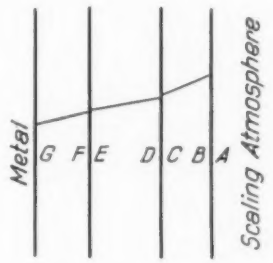

Fig. 10 — Illustrating Degree of Oxidation of Metal Surface.

in the outside surface of the Fe_2O_3 and at the metal scale interface. Due to the layer formation, however, the overall concentration gradient actually consists of several gradients. This is illustrated in Fig. 10. The molecules of the oxidizing gas strike the surface A and are absorbed, building up a definite concentration at B, the maximum concentration possible being saturation. A definite gradient exists from B to C which constitutes the driving force of the outside layer. The oxygen must pass from C to D either by diffusion or reaction. If the nature of the middle layer is such that the solubility of oxygen is lower than in the outside layer, it will not be capable of absorbing the oxygen at D as fast as it reaches C. Therefore the concentration at C will build up, which in turn causes the driving force from B to C to decrease. This reduces the amount of oxygen reaching C. A balance between the amount of oxygen arriving at C and that being absorbed at D is finally reached, when the process settles down to a steady state. Since it has been postulated that the solubility is lower in the middle layer, the concentration gradient for this layer is necessarily small. The manner of transfer of oxygen from E to F is the same as from C to D and another gradient exists from F to G. The concentration at E controls the concentration at F as it would be impossible for the

oxygen to diffuse from E to F if the concentration at F exceeded that at E. In this illustration the middle layer has been made the controlling influence on the driving force, but any of the three layers could be of such a nature so as to control the concentration gradient. Any change in the magnitude of the coefficient of diffusion will affect the scaling losses. There are two factors that affect the coefficient of diffusion; changes in temperature, and changes in the membrane through which diffusion is taking place. An increase in temperature causes an increase in the magnitude of the coefficient, and follows the expression $D\delta T^x$, where D is the diffusivity coefficient, T the temperature and x is an exponent. Changes in the character of the membrane have a definite influence on the magnitude of the diffusivity coefficient. That changes in structure of the scale membrane occur at different temperatures, these changes being confirmed by the chemical analysis of the scale formed, has been previously pointed out. It is evident that the effect of the change in the membrane must be greater than the effect of the increasing temperature on the coefficient of diffusivity to produce the phenomena of the reversal in the temperature scaling curve.

Character of Scale Membrane

A change in the structure of the membrane through which diffusion is taking place, it is thus apparent can materially alter the rate of diffusion through a change in both the concentration gradient and the diffusivity coefficient. It now remains to be shown that the above conditions occur in the scaling of steel. The equilibrium system for iron and oxygen as proposed by Pfeil (9) is given in Fig. 11. In the temperature region studied in this investigation 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.) the phases that may be present are Fe + FeO, FeO, FeO + Fe_3O_4, Fe_3O_4, Fe_3O_4 + Fe_2O_3, Fe_2O_3. From the diagram it is clearly evident that in actual scale formation the phases which are encountered are not the compounds but actually the solid solutions of FeO, Fe_3O_4 and Fe_2O_3. In fact, without the solid solution formation, concentration gradients would be reduced to zero and continuation of scaling would not be possible but would stop as soon as a film of scale was formed on the metal surface. The extent of the solid solubility at any temperature naturally varies with the different phases. The oxygen content of the scale will then not only vary from a high concentration

at the scale surface to a low concentration at the metal scale interface but also within each of the phases present. The FeO must necessarily be the phase of lowest oxygen content when not dealing with conditions permitting eutectic formation, unless it may be assumed that preferred oxidation may occur, when FeO and Fe will exist together. Since the scale forms in layers, each of these phases which

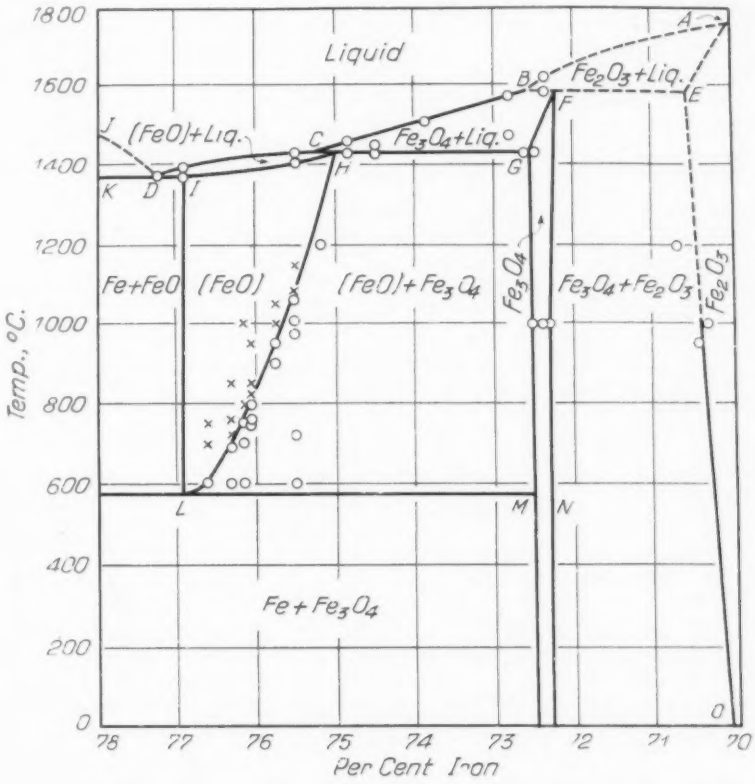

Fig. 11—Equilibrium Diagram of the Iron-Oxygen System from 70 to 78 Per Cent Iron.

are present in any one layer will show a variation in composition, the oxygen-rich concentration always being farthest from the metal scale interface. This difference in chemical composition from one side of the scale layer to the other constitutes the driving force for the diffusional process. A similar gradient exists for the iron concentration, the highest iron content being nearest to the metal scale interface.

Recent work of Jette and Foote on the Fe-O system (Fig. 12) shows the oxygen-rich boundary of the FeO field to reach a maximum at 2010 degrees Fahr. (1100 degrees Cent.). Consideration of their data indicates that this maximum could have been placed nearer

1830 degrees Fahr. (1000 degrees Cent.) without misinterpreting their results. This would point to a maximum solubility for oxygen in FeO solid solution at practically the same temperature as that at which the maximum oxidation loss is observed in the scaling of steel in air, namely 1850 degrees Fahr. (1010 degrees Cent.). The inference that the maximum scaling loss occurs at this temperature

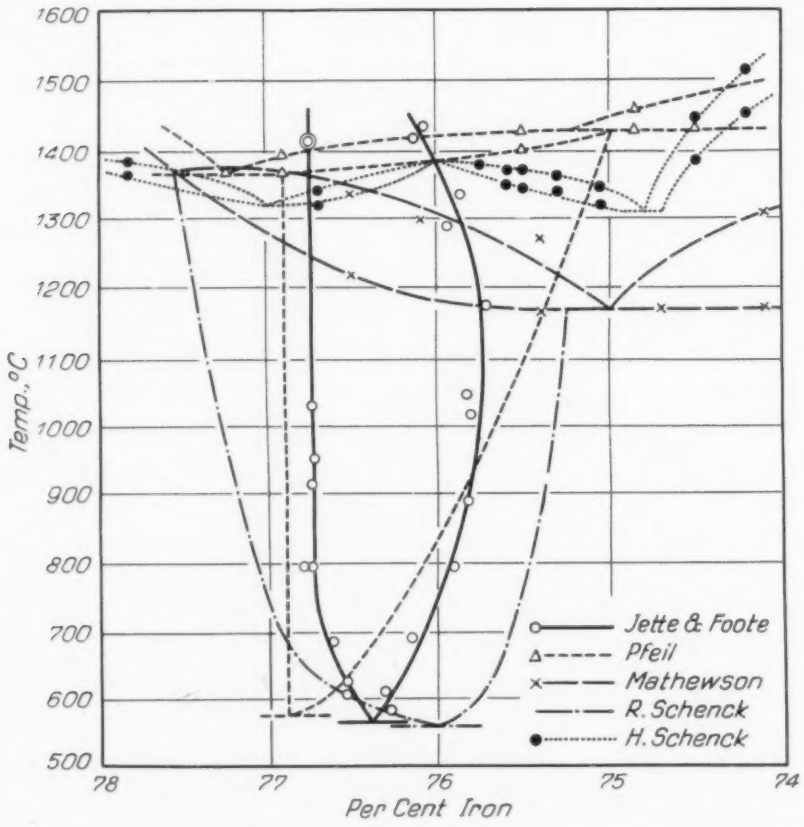

Fig. 12—Wüstite Ranges in the Iron-Oxygen System.

solely because of the maximum solubility should not be drawn as the other factors enter in. At the same time the possibility that the condition of maximum solubility allows for a maximum concentration gradient perhaps should not be ignored.

On the basis that the concentration gradient is directly influenced by the extent of the solid solubility, it follows that the phase having the lowest solubility will exert the greatest influence on the overall rate of diffusion. The amount of this phase present will also be a determining factor as the maximum concentration gradient is set by the limit of solid solubility and increasing the thickness of this phase

of the membrane causes a decrease in the gradient per unit of thickness. The Fe_3O_4 solid solution has the lowest solubility range of all the phases theoretically possible in scale formation within the temperature limits used in this investigation, 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.). It would therefore be expected that the scale formed in the temperature regions where a reversal occurs should show a relatively high proportion of Fe_3O_4 solid solution.

The chemical analyses of the scales formed at different temperatures show that the ratios of ferrous to ferric iron have a wide range of values. The ferrous iron content is relatively high at the temperature where a maximum scaling loss is obtained when compared with the ferrous iron content at the temperature where a minimum loss is obtained. At the same time the ferric iron content of the scale formed at the temperature where a maximum is reached is relatively low when compared to the ferric iron content of the scale formed at the temperature where a minimum loss is obtained. The ferric iron content, however, can exist in two of the solid solutions present, Fe_3O_4 and Fe_2O_3. Considering the Fe_3O_4 as one molecule of Fe_2O_3 and one molecule of FeO, then two thirds of the iron in the Fe_3O_4 is in the trivalent state and one third in the divalent state.

Chemical analysis and micro examinations of the scales formed under the various conditions offer means of determining the character of the scale membrane, that is the nature of the phases and the extent to which they are present. Calculations based on the analysis of the scale and the assumption that the theoretical compounds FeO, Fe_2O_3 and Fe_3O_4 are formed permit the estimation of the maximum amount of the Fe_3O_4 which could be present under any condition. A calculation of this nature which makes no allowance for any ferric iron being present as Fe_2O_3, but rather assumes all trivalent iron present at Fe_3O_4, proves a useful aid in the interpretation of the scale photomicrographs. Data from such calculations based on chemical analysis of scale formed in air in four hour runs are given in Table I. The first two columns give the ferrous and ferric iron contents of the scale analysis. In the third column the amount of ferrous iron necessary to combine with all of the ferric iron to form Fe_3O_4 is given. The fourth column shows the difference between the ferrous iron required to form Fe_3O_4 and the divalent iron content of the analysis. A minus sign denotes a deficiency and a plus sign denotes a surplus of divalent iron, that is, the sign indicates whether or not a suf-

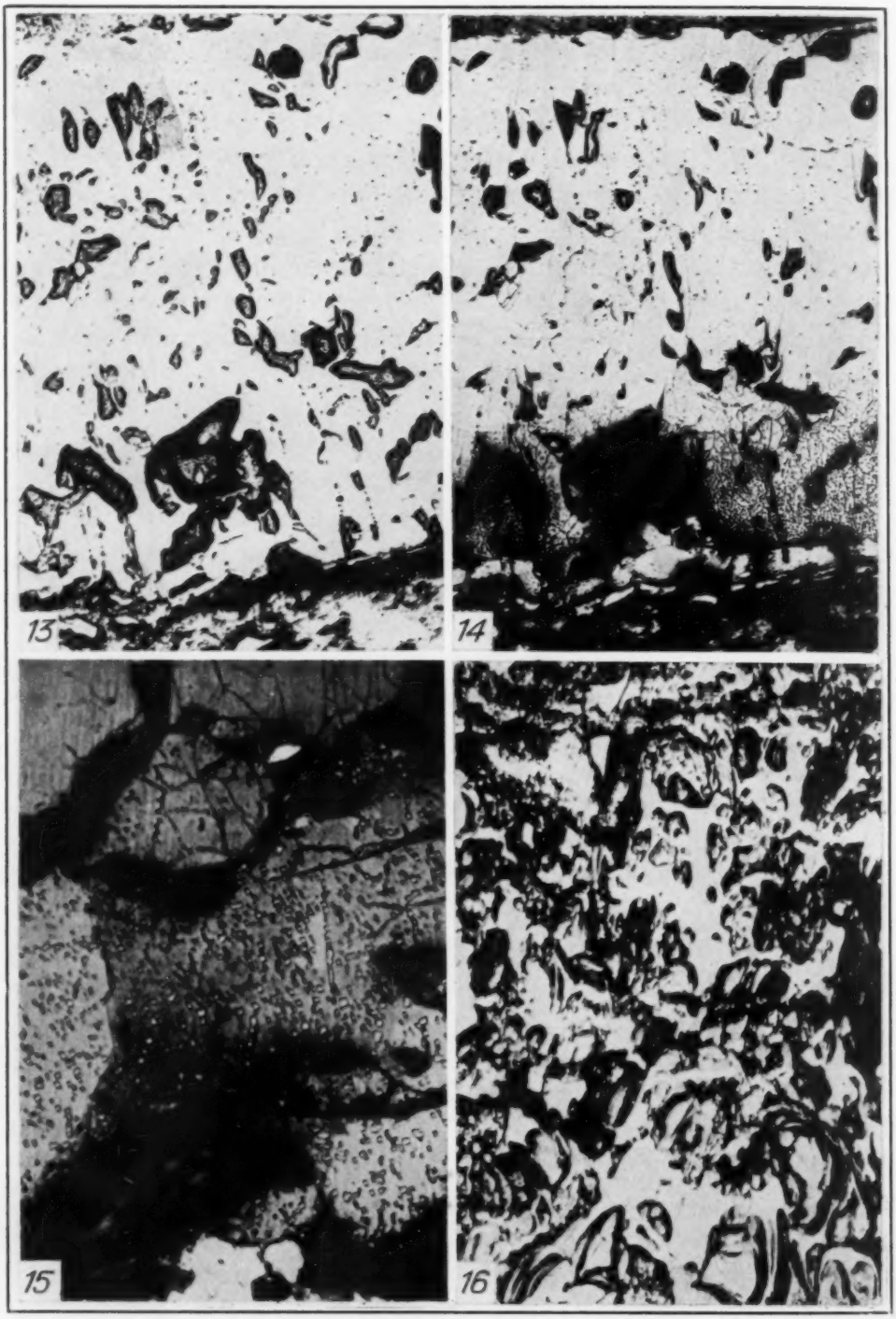

Fig. 13—Scale Formed at 1800 Degrees Fahr. Unetched. × 100.
Fig. 14—Scale Formed at 1800 Degrees Fahr. Etched in 5 Per Cent HCl in Alcohol. × 100.
Fig. 15—Precipitated Phase of the Middle Layer of Fig. 14. × 500.
Fig. 16—Scale Formed at 1915 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. × 100.

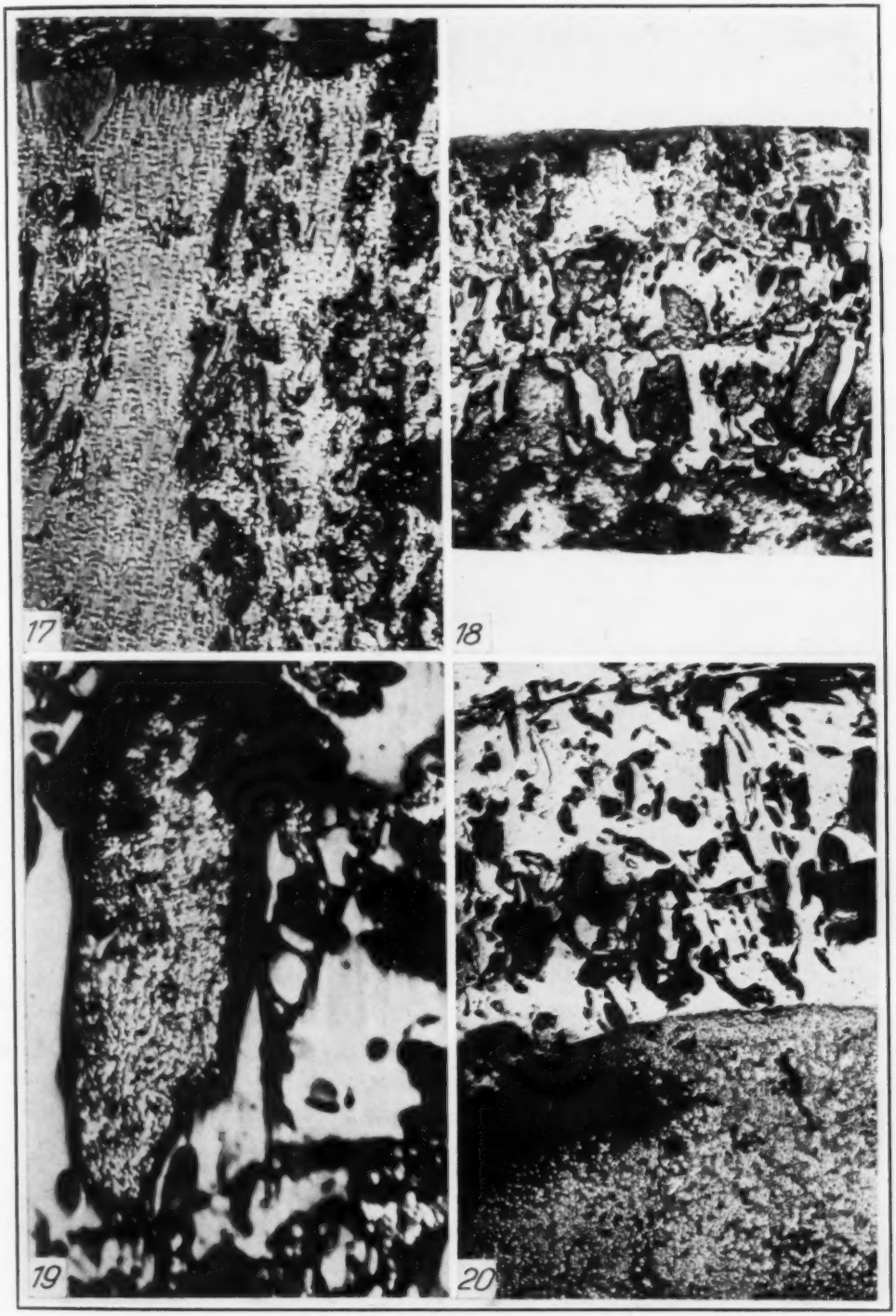

Fig. 17—Inner Layer of Scale Shown in Fig. 16. × 500.
Fig. 18—Scale Formed at 2000 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. × 100.
Fig. 19—Columnar Structure of Inner Layer of Fig. 18. × 500.
Fig. 20—Scale Formed at 2100 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. × 100.

Table I
Analysis of Scale Formed in Air in 4-Hour Runs

Temp. °F.	Fe^{++}	Fe^{+++}	Fe^{++} for Fe_3O_4	Difference of Fe^{++} Content
1800	51.80	22.05	11.02	+ 40.78
1915	34.00	39.00	19.50	+ 14.5
2000	21.50	49.40	24.70	− 3.20
2100	31.10	41.60	20.80	+ 10.30

ficient amount of ferrous iron is present in the scale analysis to combine with all of the Fe^{+++} to form Fe_3O_4. These particular analyses are given as they correspond to the samples of scale used for the photomicrographs.

Structure of the Scale

The microstructures of the cross section of the scales formed are shown in Figs. 13 through 21. These cross sections are portions of scales which were split off the steel during the quenching operation. Quenching was resorted to in order to retain as far as possible the phase present at the actual temperature of scaling. Great difficulty was encountered in the polishing of the scale due to the brittleness and it was found impossible to entirely prevent some sections from breaking away and leaving voids.

Fig. 13 shows the scale formed at 1800 degrees Fahr. (980 degrees Cent.) in the unetched condition. This same section is shown in the etched condition in Fig. 14. Three layers are evident in Fig. 13, the middle layer comprising approximately 75 per cent of the total cross section; the outside layer being 5 per cent and the inside layer approximately 20 per cent of the area. Upon etching a fine dispersion appears in the middle layer, leaving another narrow layer in relief between the inside and the fine dispersion. This finely divided dispersion is shown at higher magnification in Fig. 15 and corresponds to the decomposed ferrous state postulated by Pfeil. The decomposition of the FeO solid solution results from a decreasing solubility with decreasing temperatures. From the relationship given in Table I it is evident that an excess of FeO will exist at this temperature. Since the specific gravities of FeO, Fe_3O_4 and Fe_2O_3 are so nearly alike, namely 5.28, 5.20, and 5.12 respectively, it follows that the specific volumes of the different oxides are approximately equal; also, the total iron contents of the various solid solutions of FeO, Fe_3O_4, and Fe_2O_3 cannot vary by more than 7.78 per cent if the

theoretical compounds are formed. This difference will actually be less, due to the solid solution formation. Therefore, in order to get a qualitative relationship to establish the identity of the various layers, it may be assumed that the width of a given layer is independent of the type of solid solution present. The evaluation of the

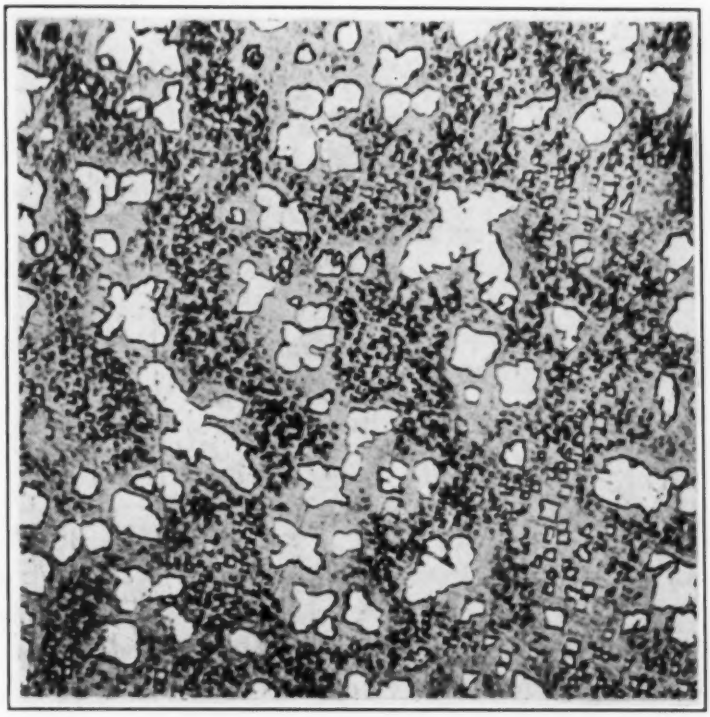

Fig. 21—Inner Layer of Fig. 20. × 1000.

consitution of the various layers may now be undertaken. It has already been pointed out that the middle layer of the scale formed at 1800 degrees Fahr. (980 degrees Cent.) (Fig. 13) comprises approximately 75 per cent of the cross sectional area. From Table I it can be seen that an excess of 40.78 per cent ferrous iron exists which represents 55.5 per cent of the total iron. This immediately establishes the fact that more than one half of the cross section must be the ferrous state. Furthermore, as Jette and Foote have shown that the oxygen-rich solid solution of FeO is composed of Fe_3O_4 dissolved in FeO, an even greater percentage of the cross sectional area must actually be present as the ferrous phase. It therefore follows that the middle layer must be composed of the ferrous phase. If the layer formation is characterized by a progressive change in phases accompanying an increase in the iron content as shown in

Fig. 11, then the outside layer must be a mixture of FeO + Fe_3O_4. Examination of this layer at high magnification showed this to be the case. It is, however, entirely possible that minute layers of the other phases out to Fe_2O_3 exist on the outside surface of the scale which were not detected in the present investigation. The inside layer should then be a mixture of Fe + FeO solid solution, not in the eutectic mixture as it is formed below the eutectic temperature, but present as a mixture nevertheless.

The formation of a mixture of Fe + FeO undoubtedly occurs when the metal surface is undergoing oxidation due to preferential oxidation, but it is difficult to conceive that the oxidation agent will pass this iron in the Fe-FeO mixture on its way to the metal scale interface, without oxidizing it to FeO. Also as the FeO solid solution in the mixture gets richer in oxygen, it will have a decided tendency to dissolve this Fe. Since there is a diffusion of iron taking place, it is possible that the iron of this mixture is taken up by the FeO and the original space occupied by the free iron is not completely filled with oxide, permitting voids to develop. This inside layer (Fig. 13) appears very spongy, suggesting that the above actually does occur. Therefore this layer would be composed of the ferrous phase as is the middle layer (Fig. 13). Two layers composed of the same phase are possible as they have different physical constructions.

Pfeil has demonstrated that the interface of the middle and inner layers represents the original metal surface before oxidation began. This has been confirmed in the present investigation. If the spongy nature of the inner layer is due to the postulations given above, then this offers a possible explanation of why this interface of the inner and middle layers represents the original position of the metal surface before oxidation. Also since the voids do not have a tendency to close, it offers an explanation for this boundary not shifting with continued oxidation. The appearance of the precipitation in the middle layer and the occurrence of the narrow band between the middle and inner layers (Fig. 13) can only be accounted for on the basis of a tempering action. As has been pointed out, the scale split away from the metal on quenching, but did not always become dislodged immediately. Therefore the heat coming out of the steel had to pass partially through this scale while it still was in contact with the steel. This tempering effect could easily cause a precipitation to take place. There is a decreasing solubility with decreasing tem-

perature in the FeC solid solution range. Since the oxygen content of any layer varies from end to end, a critical oxygen content combined with a critical tempering temperature could cause the precipitation to occur at an intermediate place as shown in Fig. 13. This phenomenon was not observed in all cases of scale formed at 1800 degrees Fahr. (980 degrees Cent.).

The scale formed at 1915 degrees Fahr. (1045 degrees Cent.) is shown in Figs. 16 and 17. From Table I it can be seen that there is an excess of ferrous iron over the amount necessary to combine with all of the ferric iron to form Fe_3O_4. This insures the presence of the ferrous phase. Fig. 16 shows that three layers are present, and an examination of the inside layer at a higher magnification (Fig. 17) shows that this layer is made up of a mixture of the FeO and Fe_3O_4 solid solutions. This then establishes the identity of the middle layer as the Fe_3O_4 solid solution and the outside layer as a mixture of Fe_3O_4 and Fe_2O_3. When the scaled sample is quenched some scale always adheres to the steel, the splitting away of the oxide always occurring some place in the scale itself. In this case the parting of the scale occurred either at the interface representing the original metal surface, or else in the inner layer shown in the photomicrographs. This is indicated by the fact that no spongy layer exists. At 1915 degrees Fahr. (1045 degrees Cent.) the scaling loss is definitely decreasing with increasing temperature (Fig. 1) and it has also been shown that the Fe_3O_4 solid solution is appearing to an appreciable extent.

The scale formed at 2000 degrees Fahr. (1095 degrees Cent.) is shown in Figs. 18 and 19. Four layers are evident in Fig. 18. The inside layer is spongy and examination at higher magnification shows that it is composed of FeO + Fe_3O_4. The next layer following the inside layer is still composed of the FeO-Fe_3O_4 mixture but the Fe_3O_4 solid solution is more prominent. The white columnar crystals are Fe_3O_4 and the mottled crystals are a mixture of FeO and Fe_3O_4. This layer is shown at a higher magnification in Fig. 19. The next layer is the Fe_3O_4 solid solution and the outside layer is comprised of a mixture of Fe_3O_4 and Fe_2O_3.

The minimum scaling loss in the region of the reversal is attained at the temperature of 2000 degrees Fahr. (1095 degrees Cent.). It has been previously pointed out that at 1915 degrees Fahr. (1045 degrees Cent.) the scaling loss was definitely decreasing and that the Fe_3O_4 solution was appearing in the scale to an appreci-

able extent. It has now been shown that at 2000 degrees Fahr. (1095 degrees Cent.) the Fe_3O_4 content has increased to still greater extent. Furthermore, it may be pointed out that the spongy inside layer is composed of a mixture of FeO + Fe_3O_4 which is high in Fe_3O_4 as compared with the inside layer of the scale in Fig. 13. Therefore the retardation in the diffusional process is not only brought about by this spongy mass which breaks up the continuity of the membrane, but also by the fact that the available mass of this material capable of allowing diffusion to take place is high in Fe_3O_4.

The structure of the scale formed at 2100 degrees Fahr. (1150 degrees Cent.) is shown in Figs. 20 and 21. The inner layer (Fig. 20) is composed of a mixture of FeO + Fe_3O_4, which is shown at a higher magnification in Fig. 21. In this case some of the magnetite particles have grown to considerable size. From Table I it can be seen that some excess ferrous phase must exist and it comprises the matrix of the inner layer. The middle layer is Fe_3O_4 solid solution and the outer layer a mixture of Fe_3O_4 and Fe_2O_3. The Fe_3O_4 content is still relatively high at this temperature (2100 degrees Fahr.) and yet the loss in weight is again increasing with increasing temperatures. This can be accounted for by the fact that the spongy layers which adhered to the metal on quenching, cannot be Fe_3O_4 as it was in the scale formed at 2000 degrees Fahr. (1095 degrees Cent.). This is necessarily true as the inside layer (Fig. 20) is composed of the decomposed ferrous phase and the spongy layer must be composed of either the decomposed ferrous phase or a phase higher in iron content. In addition the solubility range of the Fe_3O_4 solid solution begins to increase in this temperature region as can be seen from Fig. 11. It may also be pointed out that if no increase in the amount of Fe_3O_4 over that formed at 2000 degrees Fahr. (1095 degrees Cent.) occurred, and if the membrane at these two temperatures were identical, the scaling loss at 2100 degrees Fahr. (1150 degrees Cent.) would still be larger due to the increase in the diffusivity coefficient with temperature. The structure of the membrane itself influences the magnitude of the coefficient of diffusivity, but it is impossible to draw any definite conclusions regarding this from the data available at the present time.

Summary and Conclusions

The results of this investigation have shown that:

1. A reversal, that is, a decrease in the amount of scaling with increasing temperature occurs from very low oxygen concentrations to 100 per cent oxygen in the temperature range 1850 to 2000 degrees Fahr. (1010-1095 degrees Cent.).

2. The ferrous iron content of the scales formed undergoes a similar reversal, maximum and minimum occurring under approximately the same conditions as for the occurrence of the maximum and minimum for scaling.

3. The reversal occurs for all periods of time up to six hours, the maximum time period used. For a 13 per cent oxygen atmosphere the extent of the reversal was increasing with increasing time at the end of four hours.

4. The effect of increasing time on scaling in atmospheres of oxygen, air, and 13 per cent oxygen is in general the same regardless of whether or not the temperature is one at which the scaling is continuously increasing with increasing temperatures or one at which the reverse conditions exist. The 100 per cent oxygen atmosphere shows the least retardation in scaling as the time increases.

5. For those temperatures which show the greatest retardation in the rate of scaling with increase in time, the ferrous iron content of the scale is found to decrease. For those temperatures which show a less marked falling off in scaling the ferrous iron content of the scales is found to increase with time.

6. For certain oxygen concentrations the scaling losses and the ferrous iron content of the scales may remain practically constant over a given range of temperature, that is, retardation of scaling with increasing temperature may occur without a change in the degree of oxidation.

7. The change in the degree of oxidation causes a change in the membrane structure resulting in an increasing proportion of Fe_3O_4 solid solution in the temperature region where the reversal occurs.

8. The Fe_3O_4 solid solution has the lowest solid solubility range of the phases possible in the scaling system. This solid solubility is a limiting factor governing the concentration gradient or driving potential in the diffusional process. This, in turn, directly influences the rate of diffusion, the lower the driving force the lower the rate of diffusion, all other things being equal.

9. The membrane structure has a direct influence on the magnitude of the diffusivity coefficient. If the changes in the membrane

structure in the region of the reversal are of such a nature that an increase in the diffusivity coefficient results, then the effect of the lower oxygen solubility in the Fe_3O_4 solid solution must be so great that it will overcome the effect of increasing the coefficient of diffusion. On the other hand if the change in membrane structure causes a decrease in the magnitude of the diffusivity coefficient, it will be one of the contributing factors in the reversal in the temperature-loss in weight curve.

10. A theory has been advanced for the occurrence of a reversal in the temperature-loss in weight curves in the temperature region 1800 to 2100 degrees Fahr. (980-1150 degrees Cent.).

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9. L. B. Pfeil, "The Oxidation of Iron and Steel at High Temperatures," *Journal,* Iron and Steel Institute, 1929, Vol. 119, p. 501.
10. Clair Upthegrove and D. W. Murphy (Ibid).
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13. Messrs. Jette and Foote, Preprint, American Institute of Mining and Metallurgical Engineers, 1933.

DISCUSSION

Written Discussion: By A. M. Steever, vice-president and technical director, Lindberg Steel Treating Company, Chicago.

The general question of oxidation of steel has not received sufficient attention and I welcome the authors' paper as a valuable contribution upon this subject. Personally I have not carried out any research work on this subject

but have observed the problems of oxidation particularly in the forging industry.

This piece of research supplements various other contributions at different temperatures. It also co-ordinates the results of these others and appears to be a very close preliminary to some practical observations, conclusions, and recommendations which will be of value to the steel industry. From my close connection and from my experience with and in the forging industry, I can see some practical applications looming in the near future. The temperature range (1650 to 2100 degrees Fahr.) is below the mean forging temperature of S.A.E. 1020 steel. It is possible to predict effects of various atmospheres on scaling at a mean forging temperature of 2250 degrees Fahr. It would be interesting to know the results in a temperature range of 2000 to 2450 degrees Fahr. I sincerely hope the authors continue their research upon this problem and will at some future time be able to give some information as to the control of scale at these higher temperatures.

Written Discussion: By K. Heindlhofer and B. M. Larsen, U. S. Steel Corporation, Research Laboratory, Kearny, N. J.

The rate of scaling of metals has been studied by several investigators[1] with concordant results which are in accord with the picture that the rate of the scale process is determined by the rate of diffusion through the scale layer already formed, for a number of pure metals and for some alloys. In particular for the pure metals so long as the scale is continuous and adherent, the scaling rate at constant temperature tends generally to be proportional to the square root of the elapsed time at that temperature, as would be expected if the process were one of simple interdiffusion through the scale. Moreover, the variation of rate with temperature follows closely a very common and fundamental relation of the form,

$$W = k\, e^{-\frac{Q}{RT}}$$

These relationships, of course, only hold strictly under certain "ideal conditions" most important of which are that (1) oxygen must be supplied to the outer surface so abundantly as to maintain an oxygen pressure greater than the dissociation pressure of Fe_2O_3, or whatever oxide is present in this zone; (2) the scale layer (or layers) must be solid and continuous, and (3) the inner surface of the scale must be in perfect contact with the metal so the latter will also be supplied as fast as it can be absorbed into the scale.

This simple picture of the scaling process, although supported quite convincingly by all the references[1] is not in agreement with the data by Messrs. Siebert and Upthegrove, or with the previous results obtained by Upthegrove and Murphy. We therefore considered it necessary to check the data given in this paper by conducting three scaling experiments in air on ingot iron at 1860, 2012 and 2100 degrees Fahr., which corresponds to the maximum, mini-

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K. Heindlhofer and B. M. Larsen, "Rates of Scale Formation on Iron and a Few of Its Alloys." TRANSACTIONS, American Society for Steel Treating, Vol. 21, 1933, p. 865-95.

mum and end point on the solid curve in Fig. 1, shown in the authors' present paper.

The experimental procedure was essentially that described in our earlier paper on scaling (Ref. No. 1), except that we placed the thermocouple junction adjacent to rather than inside the specimen. Due to rapid oxidation in this high temperature range, we had found that the specimen tends to heat up to around 25 to 50 degrees Fahr. above the furnace temperature and for most accurate results the control couple should be placed inside the specimen. However, the present authors had apparently used the former method, and we endeavored to imitate their conditions in this respect.

Fig. A (in this discussion) shows the results of our check measurements, the vertical scale representing the weight of oxygen absorbed per unit area and the horizontal scale the time, with logarithmic scales for both variables. The

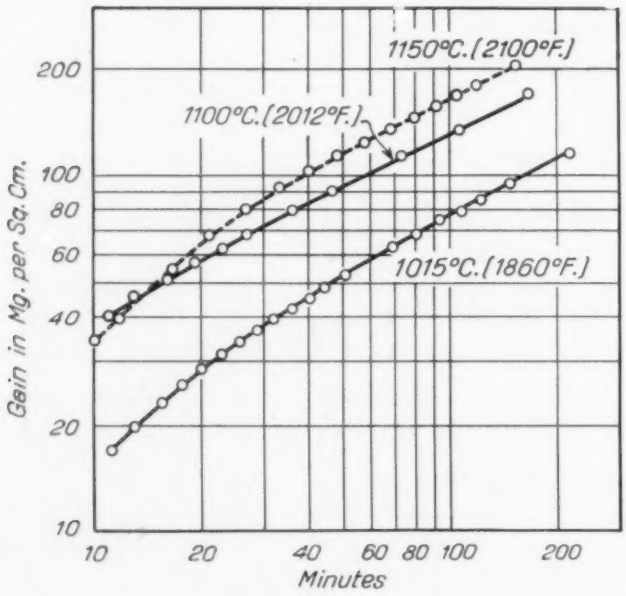

Fig. A

weight at 60 minutes is then replotted against temperature as shown in Fig. B the three points thus obtained being connected with a dotted line while the authors' results given in their Fig. 1 are reproduced for comparison as a solid line. Evidently the dip in the rate of scaling shown by the authors could not be verified, hence their results cannot be considered as typical. Analysis of the scale layers formed in these check runs for FeO shows 56.8 per cent ferrous iron for both the 1860 and 2012 degrees Fahr. scaling temperatures and 55 per cent for the scale formed at 2100 degrees Fahr. which again is contrary to the authors' results shown in their Fig. 2.

Does not the disturbing effect of increasingly widespread blistering in the scale layer seem the obvious explanation for this curious anomaly in the scaling rate-temperature curve obtained by the authors of this paper? Any blistering will tend to lift the inner layer of scale out of contact with the metal, cutting off the supply of iron by diffusion from below, but allowing continued diffusion

of oxygen in from the gas phase. The natural results of increasing blistering will be an increasing departure below the ideal rate curve, accompanied by a decreasing percentage of ferrous iron in the resulting scale, both of which effects are shown in this paper.

Attention should perhaps also be drawn to the fact that under the ideal conditions as defined above, the percentage of oxygen in the gas phase (as long as it is above a very low minimum value) should have no effect on the rate of scaling at a given constant temperature in the scale layer. The quali-

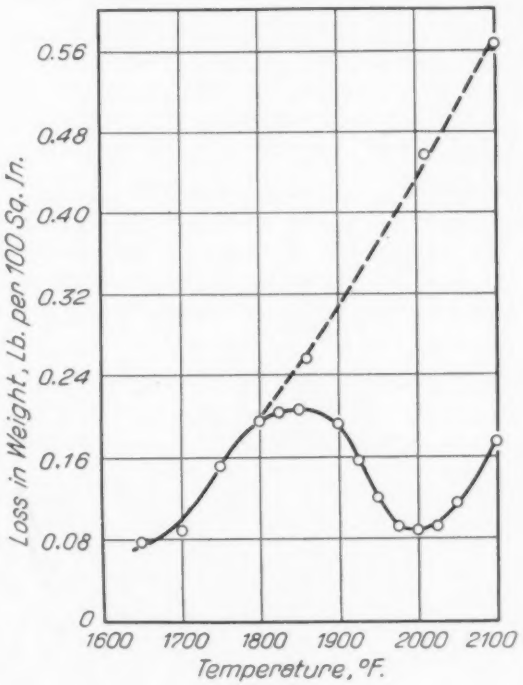

Fig. B

tative diagram Fig. 9 is thus fundamentally incorrect, the per cent oxygen scale having no significance within the range shown. These ideas are in fact supported by the data in this paper (Figs. 7 and 8) for those temperatures (1650, 1750, 1800 and 1850 degrees Fahr.) below the range of anomalous results, at which blistering was probably a negligible factor. In general it seems that the data given in this paper really represent rates for a heterogeneous diffusion system with the boundary conditions not accurately defined, and therefore are not generally applicable, either for a better scientific understanding of the problem or for predicting scaling rates under a given set of conditions.

It is of course true that most of such problems involving reaction or diffusion rates in heterogeneous systems are difficult and often impossible to treat quantitatively. The best we can ordinarily do is to try to study the "ideal rates" under certain accurately definable boundary conditions, and then frankly admit that where such accurately definable conditions are not fulfilled it will not be possible to predict results with much accuracy. In the scaling of metals, about the best we can do is to measure in the laboratory the "limiting rates"

under definite boundary conditions such as those postulated above. These will then be the maximum rates at which a certain scale layer can grow by itself by simple diffusion. If in a given practical case, we have blistering of the scale or an oxygen supply from the gas phase of less than the scale can absorb, the overall rate of scaling will be less than expected, or, if the scale cracks away periodically or the temperature of a thin sample with large surface area rises much above that of its surroundings due to the heat of combustion of the metal, the overall rate will be greater than expected. In all such cases, the laboratory data will serve at least as a general guide, but in order for it to be useful as such, we must make very certain, by logical, mathematical analysis and repeated checking of data, that the laboratory results are obtained under accurately known and defined conditions. It seems to us that this is not true of the data in the paper under discussion.

Written Discussion: By H. H. Ashdown, consulting metallurgist, Northlyn, 186 Hale Road, Hale, Cheshire, England.

It has been the privilege of the writer to discuss the other papers on oxidation and scaling presented by Mr. Upthegrove and his associates at previous conventions and I suggest this paper is a further contribution to the series. I mention series as I believe these papers have opened up a wide field for research.

This paper in itself is a valuable piece of research work and the authors are to be congratulated on their determination to find the reason for the apparent abnormal rate of oxidation within the range of 1800 and 1900 degrees Fahr. (985 to 1040 degrees Cent.).

This is extremely valuable information to mill and forge superintendents, particularly those who are dealing with large mill production or who are responsible for the handling of large masses of steel which require long periods of soaking at high temperatures.

The diagrammatic sketch on page 200 is an excellent presentation of the scaling procedure, indicating that ingots or billets should first receive an initial soaking at 1800 degrees Fahr. and then be rapidly heated to, and soaked at around 2100 degrees Fahr. for rolling or forging. The scale losses on forgings may not be generally appreciated. Forgings today are made up to 100 tons weight, and if we assume the scaling loss to be 5 per cent, which is a low estimate, five tons of valuable steel, and usually the best portion of the steel, becomes a total loss.

Valuable as this paper is, I believe its value might have been considerably enhanced had the authors given photomicrographs of the steel quenched with the scale, at temperatures of 1800, 1850 and 2100 degrees Fahr.

The authors call attention to the increasing percentage of iron in the scale at 2100 degrees Fahr. It is to be observed that during long soaking periods at high temperatures the ferrite appears to become divorced, diffusing outward in increasingly wide bands. This, apart from the scale reaction with the carbon content of the steel, may account for the increased iron content. This was clearly indicated in the photograph I contributed to the paper by Murphy, Wood and Jominy in 1932, which showed in the scale, on the base of a 70-inch octagonal ingot, which had been soaked for a long period at around 2200 degrees

Fahr., large, broad pentagonal boundaries of much lighter color, corresponding with the ferrite.

Since reading this paper, I am of the opinion that just as the condition of the slag of the open-hearth furnace is a criterion of the character of the steel in the bath, so the type of scale on the billet will give an index to certain physical properties which may be expected from the finished forging. I believe some correlation between the scale and steel will be found to exist, not only at the interface of the scale and metal, but throughout the mass of the steel under treatment. Further, this may give a solution to some of the "banded" steel problems.

If I might offer a suggestion for further investigation, I would suggest six, 4-inch billets be taken—two heated to 1800 degrees Fahr., two to 1850 degrees Fahr. and two to 2100 degrees Fahr. In each case, one quenched for scale and steel structural examination and the other rolled or forged and examined for structural and physical properties.

The work already done by the authors has been of great value to the steel industry and it is hoped that funds will be forthcoming to encourage them to continue this line of research. First, to further investigate controlled atmospheres for commercial application and reduce these enormous scale losses without detriment to the finished product. And secondly, to continue their research to determine the relationship of the type of scale as an index to the ultimate physical values of the steel.

Authors' Closure

The authors appreciate the comments of Heindlhofer and Larsen and agree heartily with their view that in order for laboratory data to be useful as such, it must be made certain by repeated checking and logical analysis that the results are obtained under accurately known and defined conditions. The use of mathematical analysis in checking experimental data is always highly desirable, but care must be exercised in the use of such analysis not to extend its application beyond the scope of the assumptions on which it is based. It would appear that Heindlhofer and Larsen are insisting on extending the application of a relationship based on an assumption of constancy of type of membrane to a condition where it has been definitely shown a change in membrane does occur.

Heindlhofer and Larsen cite the work of Pilling and Bedworth, of Dunn and their own as the basis for the statement that the variation in scaling with increase in temperature follows the fundamental relation of the form

$$W = Ke^{-\frac{Q}{RT}}$$

and consequently the variations with temperature reported here must be incorrect. The authors are not attempting in any sense to deny the validity of this relation for certain metals or ranges of temperatures, but do insist that there may be exceptions to it.

It is very interesting that Dunn,[3] cited by Heindlhofer and Larsen, shows in a later publication than the one referred to by them a departure from the straight line law. In investigating the oxidation of the brasses Dunn found that

[3]J. S. Dunn, *Journal*, Institute of Metals, Vol. 46, 1931, p. 25-48.

an 85.7 per cent copper alloy departed from the straight line law followed by the other alloys and concluded that "the alloys with copper content between 80 and 86 per cent behave in a more complex manner, which is not susceptible to mathematical analysis."

It is also interesting to note that the published results of Pilling and Bedworth, the second reference given, showed a deviation from the straight line law in the oxidation of copper in oxygen. The data of these investigators for the oxidation of copper at 900, 950 and 1000 degrees Cent. (1650, 1740, 1830 degrees Fahr.) (Figs. 26 and 27) are reproduced in Fig. 1. The oxidation is definitely less at 1000 degrees Cent. than at 900 or 950 degrees Cent. for all times up to 3 hours.

Pilling and Bedworth reported a deviation from the straight line law for oxidation of copper in air at 700 degrees Cent. (1290 degrees Fahr.), stating

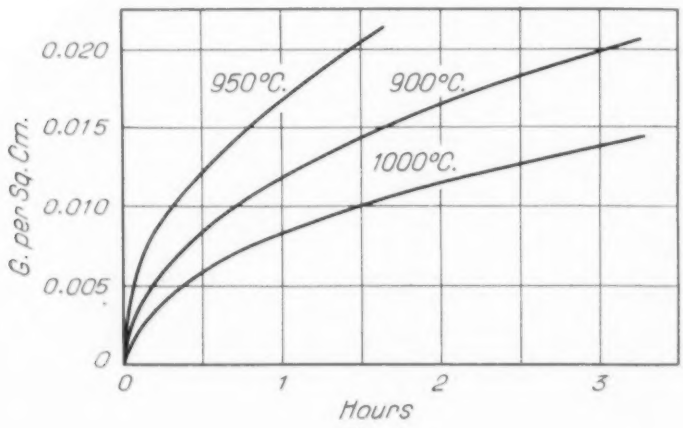

Fig. 1

"the low value at 700 degrees Cent. (1290 degrees Fahr.) has been repeatedly checked and is without satisfactory explanation." Heindlhofer and Larsen plotted the values from Pilling and Bedworth's curves for the oxidation of copper in air for 100 minutes on a Log W vs. 1/T scale. This appears to have involved the extrapolation of the data at 1000 degrees Cent. (1830 degrees Fahr.) as Pilling and Bedworth report only ½ and 1 hour runs at this temperature. A straight line was drawn through the points for 1000, 900 and 700 degrees Cent. (1830, 1650 and 1290 degrees Fahr.) (their Fig. 5), the 800 degrees Cent. (1470 degrees Fahr.) point falling above the line. The question may well be raised as to whether or not the data as plotted in their Fig. 5 should not and do not show the same deviation as reported by Pilling and Bedworth. This perhaps can best be answered by the plotting of Pilling and Bedworth's values for the scaling of copper in air for 60 minutes in Heindlhofer and Larsen's Fig. 5 (Fig. 2). The deviation from the straight line is definite and unquestionable.

The work of Cobb[3] and his associates should also be referred to in this connection. They reported scaling determinations for a low carbon steel in atmospheres of carbon dioxide and air at 900 degrees Cent. (1650 degrees Fahr.)

[3]Marson and Cobb, *Journal*, Society of Chemical Industries, Vol. 46, 1927, 61T-72T.

and 1000 degrees Cent. (1830 degrees Fahr.) for a 3-hour period as follows.

	CO_2	Air
900 degrees Cent. (1650 degrees Fahr.)	0.0016 gm./sq.cm.	0.0295 gm./sq.cm.
1000 degrees Cent. (1830 degrees Fahr.)	0.0064 gm./sq.cm.	0.0635 gm./sq.cm.

The scaling in carbon dioxide at 900 degrees Cent. (1650 degrees Fahr.) is seen to be roughly 5 per cent of the gain in weight in air and at 1000 degrees Cent. (1830 degrees Fahr.) roughly 10 per cent of that in air. These percentages are checked closely by the results obtained in these laboratories on tests on 0.20 per cent carbon steel for 2-hour periods and using loss in weight as the measure of scaling.

	CO_2	Air
900 degrees Cent. (1650 degrees Fahr.)	0.007 lbs./100 sq.in.	0.066 lbs./100 sq.in.
1000 degrees Cent. (1830 degrees Fahr.)	0.027 lbs./100 sq.in.	0.253 lbs./100 sq.in.

Here the ratio of scaling in carbon dioxide to that in air is approximately 10 per cent. Heindlhofer and Larsen, however, report for ingot iron a much

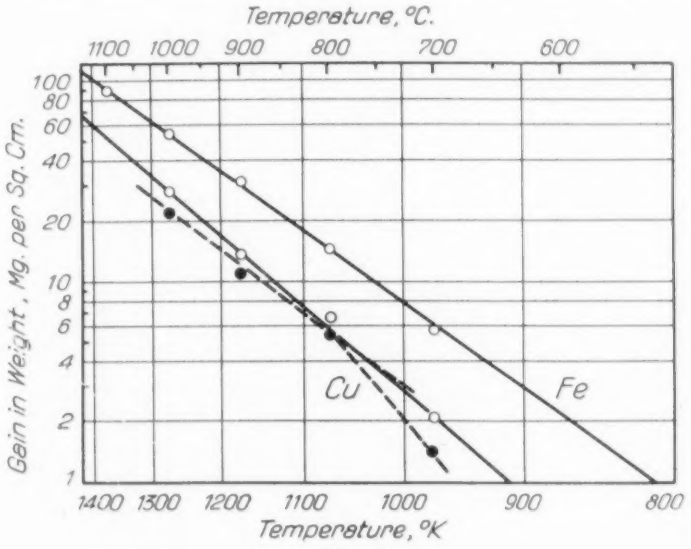

Fig. 2

higher ratio at 900 degrees Cent. (1650 degrees Fahr.) at the end of 100 minutes, namely 40 per cent. While Cobb and his associates did not carry out scaling tests at 1095 degrees Cent. (2000 degrees Fahr.) and above, such tests were carried out by Wood, Jominy and Murphy, and Murphy and Upthegrove. These tests indicated that at temperatures above 1095 degrees Cent. (2000 degrees Fahr.) air and carbon dioxide gave very similar results. The fact that at temperatures up to 1000 degrees Cent. (1830 degrees Fahr.) a carbon dioxide atmosphere produced roughly only ten per cent of the scaling produced in air, yet at temperatures over 1095 degrees Cent. (2000 degrees Fahr.) it produced scaling in a low carbon steel very similar to that in air, it would seem, points quite definitely to a discontinuity in the temperature effect for air.

Heindlhofer and Larsen have offered as evidence, that the decrease in the rate of scaling does not occur, data from single tests made at three temperatures, 1015, 1100 and 1150 degrees Cent. (1860, 2010, and 2100 degrees Fahr.),

in which they determined gain in weight at short intervals of time up to 2 hours or slightly longer. The tests were made on ingot iron rather than on 0.20 per cent carbon steel and apparently in an atomsphere using the laboratory air as the source rather than purified and dried air. No information is given as to conditions existing at the beginning of the test. While they report failure to obtain a decrease in scaling on a different material, the authors wish to point out that the decrease reported has been repeatedly checked in these laboratories over a period of three years. The tests have been checked on three different experimental set-ups, on different low carbon steels and by different observers. It would thus seem that the data were obtained under accurately known and defined conditions.

In view of Heindlhofer and Larsen's failure to confirm our results, it is of interest to compare their results on ingot iron in air at 1015 degrees Cent. with those of Cobb and his associates on a low carbon steel at 1000 degrees Cent. For a 3-hour period, in which both used the gain in weight method and the thermocouple external to the specimen, Heindlhofer and Larsen obtain a gain of 0.107 gms./sq.cm. while Cobb and Angus at a temperature only 15 degrees lower obtain a gain in weight of but 0.063 gm./sq.cm. or only 60 per cent of the gain reported by the former. In the results previously presented in their paper a gain in weight of 90 mg./sq.cm. in 100 minutes at 1100 degrees Cent. (2010 degrees Fahr.) is shown for commercially pure iron. In the results presented in the discussion a gain in weight of 133 mg./sq.cm. is shown for ingot iron in 100 minutes at 1100 degrees Cent., (2010 degrees Fahr.), a difference of 50 per cent which can hardly be attributed to the position of the thermocouple.

Failure to obtain confirmation of the decrease in composition is also reported. No mention was made as to the method of obtaining the scale, that is, quenching procedure, a factor which may very definitely influence the final results. Again it should be pointed out that Heindlhofer and Larsen made these determinations on ingot iron, while the determinations of the authors and those previously reported by Upthegrove and Murphy were for 0.20 per cent carbon steels.

Heindlhofer and Larsen believe the diagram of Fig. 9 to be fundamentally incorrect. This is a matter of viewpoint based largely on the question of the character of the membrane. In fact all points in controversy come down to the question of whether or not deviations from the laws, which have been established for oxidation of certain metals and ranges of temperatures, can occur and whether or not a logical explanation for these deviations can be offered. The authors believe they have demonstrated the occurrence of such a deviation for the 0.20 per cent carbon steel and at the same time have offered an explanation not inconsistent with the laws governing diffusion processes.

The authors welcome Mr. Ashdown's very valuable and constructive comments. Attempts to retain the scale with the steel as suggested by Mr. Ashdown proved unsuccessful, the major portion always breaking away on quenching. Mr. Ashdown's suggestion that some correlation may exist between the scale and the steel, it is believed, touches on one of the very important factors underlying the scaling phenomena. The authors are at present undertaking work in this direction.

Mr. Steever's comments are acknowledged.

THE DUCTILITY OF CHROMIUM-NICKEL AUSTENITIC STEELS AT ELEVATED TEMPERATURES

By H. D. Newell

Abstract

High alloyed chromium-nickel austenitic steels are more or less non-ductile under tensional deformation at temperatures between 1000 and 1800 degrees Fahr. (540-980 degrees Cent.). This is also true of many lower alloy pearlitic steels and even open-hearth iron at temperatures corresponding to their transformation to the gamma state.

The present paper shows the effect of various special elements and of composition variation on the ductility of such austenitic steels at elevated temperatures as measured by short-time tensile tests. A few other materials are included for comparison.

It is concluded that lack of ductility is associated with the austenitic face-centered structure while the alpha iron or body-centered arrangement provides a high degree of ductility. Improvement in the elevated temperature ductility of austenitic steels, within the temperature range studied, may be brought about by the addition of elements tending to form ferrite. The element silicon seems to be an exception and improves ductility at the higher temperatures even where the structure remains wholly austenitic. Ferrite-forming elements which confer grain refinement, without stiffening the matrix, improve ductility to a greater extent than those which stiffen the matrix without greatly refining the structure. Titanium is an example of the first class and molybdenum and vanadium of the second class. The last mentioned elements increase short-time strength to a considerable degree. Contrary to expectations, a columbium addition did not improve the ductility of 18-8.

Introduction

AUSTENITIC steels of the general 18-8 type have erroneously been described as becoming brittle at elevated temperatures. As a matter of fact such steels remain extremely tough when hot

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and are fully capable of resisting sudden shocks or stresses under severe service conditions. Heating such steels in the carbide precipitation range may cause a reduction of impact strength through precipitation or structural alteration, but, in most cases, the impact strength remaining is substantial, especially in alloys of low carbon content. Most of the determinations of impact resistance have been made cold after heating, but a few tests show excellent values at elevated temperatures.[1]

Under static loading, the austenitic steels are hot-short and exhibit reduced ductility in the general temperature range 1000 to 1800 degrees Fahr. (538-982 degrees Cent.). Lester[2] has described this condition and has attributed it to formation of ferrite and precipitation of carbides along atomic planes in grains that would normally be favorable to slip. The lack of ductility or hot-shortness manifests itself under tensional deformation in the form of intergranular fracture with adjacent intergranular cracks. In a practical sense, this lack of ductility has caused difficulties in certain fabricating operations, such, for example, as tube bending and expanding or plate bending. It has also caused unfavorable comment in the refining[3] industry because 18-8 tubes do not give warning of impending failure by bulging when overheated. The condition has been alleviated by the user in correct cracking furnace design and careful operating practice, so that such failures are now a rarity. The shortcomings of the alloy, so far as ductility is concerned, are well known.

Purpose of Investigation

Feeling that any enhancement of elevated temperature ductile properties would be welcomed, a study was made of a number of experimental and commercial austenitic alloy steels. Alteration of usual composition and additions of moderate amounts of special elements were made and the resulting alloys were subjected to short-time tensile tests at temperatures extending into the reduced ductility range. The short-time tensile test was used in preference to the slow bend test because of its convenience and greater ease of

[1] R. Sergeson, "Effect of Temperature on Stainless Iron," *Heat Treating and Forging*, January 1929, p. 55.

[2] H. H. Lester, "The Brittle Range in 18 and 8 Chromium-Nickel Iron," TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 743.

[3] E. S. Dixon, "Needs of the Oil Industry for Metal at High Temperatures," Symposium on Effect of Temperature on Metals, American Society for Testing Materials—American Society of Mechanical Engineers, 1931, p. 66.

interpretation of results. Elongation and reduction of area measurements were taken as the criteria of ductility and strength values were obtained as a matter of course.

Materials and Test Procedure

The materials investigated were mainly special melts made in a 35 kva 6000 cycle high frequency furnace lined with magnesite. The melts were cast into 2⅝-inch rounded corner, square, tapered ingots weighing about thirty pounds each with hot top. The ingots were cropped by sawing, heated in a gas-fired forging furnace to 2150 degrees Fahr. (1175 degrees Cent.), and forged under a Bradley hammer to ⅞-inch diameter rounds. Several reheatings were necessary to complete the operation and the final forging from square to round section was done in swaging dies to prevent piping. Other materials tested were in the form of commercial hot-rolled ⅞ or 1-inch rounds.

Having previously determined that grain size affects elevated temperature ductility,[4] it was decided to test all materials in the fine-grained as forged or rolled condition, which condition is conducive to highest ductility as measured by the short-time test. The forged or rolled bars were turned up into 0.505-inch threaded end tensile specimens and short-time tests were made, with some exceptions, through the range 1000 to 1600 degrees Fahr. The specimens were all pulled in a screw machine at a crosshead rate of 0.08-inch per minute until rupture occurred and uniform practice was used as to heating procedure. Temperature variation did not exceed plus or minus 10 degrees Fahr., from the nominal temperature. The test method in general approximated the tentative code[5] now proposed for such testing. Composition of the steels tested is shown in Table I.

The forging practice used no doubt created some non-uniformity within the same bar or from bar to bar because of variations in finishing temperatures. For the purpose of this investigation, it is believed these effects may be discounted, especially toward the high end of the testing range.

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[4]H. D. Newell, "Influence of Grain Size on the Properties and Corrosion Resistance of the 18-8 Iron-Chromium-Nickel Alloys for Elevated Temperature Service." TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1931-32, p. 673.

[5]Tentative Methods of Test—"Short-time High-temperature Tension Tests of Metallic Materials," E-21-33T, *Proceedings*, American Society for Testing Materials, Vol. 33, Part I, p. 996.

Table I
Analyses of Steels

Steel	Modification		Composition—Per Cent C	Mn	Cr	Ni	Si	Mo	V	Ti	Cb
1	18-8 Low Carbon	(r)	0.054	0.40	18.30	9.22	0.37	.....	.....	.....	.....
2	18-8 High Carbon	(r)	0.14	0.31	17.41	9.56	0.43	.....	.....	.....	.....
3	18-8 Silicon	(r)	0.14	0.55	17.54	9.80	2.00	.....	.....	.....	.....
4	18-8 Molybdenum	(r)	0.10	0.41	17.36	8.68	0.37	3.08	.....	.....	.....
5	18-8 Columbium	(r)	0.10	....	18.38	8.97	.....	.....	.....	.....	1.16
6	25-20 Chromium-Nickel	(r)	0.10	0.52	24.96	21.00	0.97	.....	.....	.....	.....
7	18-8 Vanadium	(e)	0.18	0.42	18.53	9.04	0.30	.....	0.60	.....	.....
8	18-8 Vanadium	(e)	0.12	0.44	18.66	8.98	0.32	.....	1.15	.....	.....
9	18-8 Vanadium	(e)	0.14	0.49	18.40	8.94	0.36	.....	2.31	.....	.....
10	18-8 Titanium	(e)	0.186	0.52	19.25	9.12	0.41	.....	.....	0.21	.....
11	18-8 Titanium	(e)	0.184	0.61	19.28	9.12	0.45	.....	.....	0.44	.....
12	18-8 Titanium	(e)	0.16	0.63	19.12	9.22	0.67	.....	.....	0.88	.....
13	18-8 Titanium	(e)	0.158	0.58	19.31	9.18	0.66	.....	.....	1.90	.....
14	18-14 Chromium-Nickel	(e)	0.09	0.33	18.01	13.82	0.27	.....	.....	.....	.....
15	18-14 Chromium-Nickel-Titanium	(e)	0.12	0.39	18.11	13.46	0.32	.....	.....	0.09	.....
16	21-12 Chromium-Nickel	(e)	0.104	0.23	22.00	11.92	0.28	.....	.....	.....	.....
17	21-12 Chromium-Nickel-Titanium	(e)	0.144	0.31	20.28	11.92	0.10	.....	.....	0.12	.....
18	18-8	(e)	0.092	0.33	17.92	9.14	0.51	.....	.....	.....	.....
19	18-8 Titanium	(e)	0.116	0.32	18.63	9.02	0.49	.....	.....	0.09	.....
20	18-7 Titanium	(e)	0.06	0.43	17.62	7.03	0.83	.....	.....	0.30	.....
21	18-5 Titanium	(e)	0.11	0.40	18.31	5.17	0.60	.....	.....	0.12	.....
22	18-5	(e)	0.11	0.50	17.23	4.98	0.53	.....	.....	trace	.....
23	18-8 Titanium	(e)	0.045	0.59	16.80	8.86	0.66	.....	.....	0.21	.....
24	4-6 Per Cent Chromium-Molybdenum	(r)	0.16	0.36	5.13	.....	0.37	0.59	.....	.....	.....
25	Copper-Molybdenum O-H Iron	(r)	0.04	0.35	.....	.....	0.010	0.18	Cu. 48	.....	.....
26	18 Per Cent Chromium	(r)	0.10	0.38	17.86	0.25	0.42	.....	.....	.....	.....

(r) Commercially rolled ⅞ or 1-inch rd.
(e) Forged experimental alloys.

Test Data

Table II gives the short-time data obtained on all steels listed in the previous table. The ductility of a metal is usually considered a function of its ability to elongate and reduce itself in area under plastic deformation. In consequence, a "ductility factor" has been given each test. This factor was obtained by simply adding the per cent elongation and the per cent reduction and dividing by two. It is believed that such a ductility factor gives a good index of ductility under the conditions of test extant.

A review of the data shows, that with the single exception of silicon, which element markedly improves ductility, the ductilities of the austenitic steels are more or less alike. The addition of such elements as titanium, vanadium and molybdenum in increasing quantities develops ferrite (delta iron) which tends to improve ductility. Carbon in amounts present in the usual commercial wrought alloys seems to have little effect one way or another except when it is so low as to permit ferrite to be present or to allow additional ferrite to be generated during pulling the specimens at the lower temperatures. Vanadium appears to be less effective than titanium in increasing ductility possibly because it is not so potent in its grain refining action.

Discounting the effects of variation in carbon, chromium, nickel, etc., in the titanium and vanadium group alloys, the increases in ductility, as functions of these elements, are shown in Figs. 1 and 2.

Assuming that the ductility increase was due to increasing proportions of ferrite and not to any specific action of the added elements, it was decided to develop low temperature ferrite by the simple expedient of lowering the nickel content. This brought about other modifications in physical properties not wholly unlooked for, but tended to support the theory that increased ductility resulted from the presence of ferrite. This may be seen by reference to Fig. 3, showing ductility of ordinary 18-8 with those containing lower nickel contents. Short-time properties of silicon, molybdenum, and columbium 18-8's contrasted to commercially rolled low carbon 18-8 are shown in Fig. 4.

The amount of ferrite in the compositions investigated was not determined quantitatively, but was ascertained by tests with a needle suspended within the field of a strong permanent magnet and by examination of the microstructures. Typical photomicrographs of

Table II
Short-Time Test Data

Steel No.	Brinell (R. T.)	Temperature of Test °F.	Ultimate Lbs. Per Sq. In.	Elongation % in 2 Inch	Reduction of Area	Ductility Factor
1—18-8 Low Carbon	143	1000	54,245	67.5	43.5	55.5
		1200	38,260	58.8	57.0	57.9
		1400	32,750	71.0	49.0	60.0
	Nonmagnetic	1600	13,650	38.8	43.5	41.2
		1700	9,950	35.0	48.0	41.5
2—18-8 High Carbon	159	1000	67,200	68.3	49.5	58.9
		1200	55,300	56.1	40.0	48.15
		1400	30,900	64.6	57.5	61.05
	Nonmagnetic	1600	16,190	36.1	37.0	36.55
		1700	14,740	44.5	56.0	50.25
3—18-8 Silicon	166	1000	75,900	52.5	63.5	58.0
		1200	57,100	34.0	34.8	34.4
		1400	32,200	69.5	73.2	71.35
		1500	27,000	77.0	73.0	75.0
	Nonmagnetic	1600	18,720	80.5	76.7	78.6
		1700	14,080	87.0	77.2	82.1
4—18-8 Molybdenum	207	1000	80,040	26.5	60.8	43.65
		1200	73,200	27.0	61.4	44.2
		1400	51,420	33.0	73.5	53.25
	Magnetic	1600	32,450	39.5	81.0	60.25
		1800	26,710	60.0	84.4	72.2
5—18-8 Columbium	197	1000	62,000	23.5	61.2	42.35
		1200	51,050	28.0	56.5	42.25
		1400	36,800	22.5	39.8	31.15
		1500	32,750	22.0	46.3	34.15
	Magnetic	1600	26,090	25.0	38.9	31.95
		1700	21,650	21.0	32.5	26.75
6—25-20 Chromium-Nickel	179	1000	80,450	32.5	51.4	41.95
		1200	64,250	34.0	48.9	41.45
		1400	44,450	45.0	55.8	50.4
	Nonmagnetic	1600	24,050	46.0	47.6	46.8
		1800	11,630	54.5	46.7	50.6
7—18-8 0.60 Per Cent Vanadium	193	1000	79,500	43.0	59.6	51.3
		1200	54,100	45.0	40.7	42.85
		1400	51,900	27.5	32.5	30.0
	Nonmagnetic	1500	44,600	24.0	36.0	30.0
		1600	35,350	27.0	36.6	31.8
8—18-8 1.15 Per Cent Vanadium	175	1000	74,700	45.5	59.7	52.6
		1200	67,850	38.5	44.6	41.55
		1400	55,100	26.5	31.5	29.0
	Nonmagnetic	1500	40,600	27.0	40.7	33.85
		1600	32,150	29.5	53.4	41.5
9—18-8 2.31 Per Cent Vanadium	187	1000	77,700	37.5	47.6	42.5
		1200	71,900	34.0	41.3	37.65
		1400	55,600	27.0	31.6	29.3
	Magnetic	1500	37,350	36.5	57.9	47.2
		1600	33,400	32.0	61.0	46.5
10—18-8 0.21 Per Cent Titanium	207	1000	77,700	49.5	60.7	55.1
		1200	64,800	35.0	57.3	46.15
		1400	41,150	36.0	46.6	41.3
	Nonmagnetic	1500	34,750	32.0	38.8	35.4
		1600	26,700	21.0	35.4	28.2
11—18-8 0.44 Per Cent Titanium	202	1000	77,800	42.5	56.7	49.75
		1200	66,700	39.0	51.9	45.45
		1400	46,350	42.0	60.3	51.15
	Nonmagnetic	1500	33,200	39.0	57.8	48.4
		1600	28,150	43.5	63.3	53.4
12—18-8 0.88 Per Cent Titanium	175	1000	72,500	42.0	61.3	51.65
		1200	63,100	36.0	58.2	47.10
		1400	44,750	41.0	60.3	50.50
	Nonmagnetic	1500	32,000	46.5	71.0	58.75
		1600	26,700	46.5	74.5	60.5

Table II (Continued)
Short-Time Test Data

Steel No.	Brinell (R. T.)	Temperature of Test °F.	Ultimate Lbs. Per Sq. In.	Elongation % in 2 Inch	Reduction of Area	Ductility Factor
13—18-8 1.90 Per Cent Titanium	207	1000	74,650	27.5	61.3	44.4
		1200	59,700	32.0	62.2	47.1
		1400	38,100	51.0	68.7	59.85
	Magnetic	1500	27,500	52.5	78.9	65.7
		1600	24,850	63.5	86.2	74.85
14—18-14 Chromium-Nickel	143	1000	63,180	39.0	58.2	48.6
		1100	56,850	39.0	53.8	46.4
		1200	54,650	39.5	49.8	44.65
	Nonmagnetic	1400	34,950	38.0	42.2	40.1
		1500	27,000	36.5	32.5	34.5
15—18-14 Titanium	163	1000	72,700	43.0	60.1	51.55
		1200	60,650	37.5	50.0	43.75
		1400	35,000	28.0	36.6	32.3
	Nonmagnetic	1500	30,000	23.0	31.9	27.45
		1600	23,900	22.0	27.5	24.75
16—21-12 Chromium-Nickel	169	1000	68,750	41.0	62.1	51.55
		1200	58,250	41.5	53.0	47.25
		1400	38,250	46.5	51.4	48.7
	Nonmagnetic	1500	30,250	40.5	42.2	41.35
		1600	25,000	42.0	41.0	41.5
17—21-12 Titanium	179	1000	76,200	41.0	54.0	47.5
		1200	60,350	29.5	53.3	41.4
		1400	39,250	35.0	54.1	44.55
	Nonmagnetic	1500	31,850	30.0	53.0	41.5
		1600	28,750	24.0	43.4	33.7
18—18-8	172	1000	64,700	40.0	66.1	53.05
		1200	51,250	41.0	54.0	47.5
		1400	32,500	50.0	51.9	50.95
	Nonmagnetic	1500	23,500	38.5	47.8	43.15
		1600	20,700	35.0	24.3	29.65
19—18-8 Titanium	179	1000	67,000	42.5	64.2	53.35
		1200	54,500	41.0	58.3	49.65
		1400	36,750	45.0	50.0	47.50
	Nonmagnetic	1500	28,750	35.0	38.2	36.6
		1600	24,400	28.0	34.7	31.35
20—18-7 Titanium	207	1000	68,125	26.0	50.8	38.4
		1200	57,290	26.5	56.9	41.7
		1400	39,180	30.0	71.5	50.75
	Magnetic	1500	35,110	49.0	79.2	64.1
		1600	29,400	40.0	82.7	61.35
21—18-5 (c) 0.12 Per Cent Titanium	285	1000	81,500	26.0	53.6	39.8
		1200	45,650	60.0	84.9	72.45
		1400	36,500	46.0	71.8	58.9
	Magnetic	1500	32,450	48.0	68.4	58.2
		1600	26,450	51.5	67.8	59.65
22—18-5	363	1000	115,000	12.5	37.6	25.05
		1200	49,250	41.0	75.5	58.25
		1400	32,290	47.5	87.1	67.3
	Magnetic	1500	29,100	67.0	90.2	78.6
		1600	22,600	43.0	90.6	66.8
23—18-8 Titanium	156	1000	60,900	37.0	49.0	43.0
		1200	48,860	24.0	50.0	37.2
		1400	33,550	57.0	68.8	62.9
	Nonmagnetic	1500	30,150	50.5	70.4	60.4
		1600	24,800	56.0	73.5	64.7
24—4-6 Per Cent Chromium-Molybdenum	143	1000	45,350	46.0	83.2	64.6
		1200	24,450	69.5	93.7	81.6
		1400	11,370	78.0	98.8	88.4
		1500*	11,890	22.5	73.5	48.0
	Magnetic	1600	12,940	41.5	50.2	45.85
		1700	9,950	41.5	49.5	45.5

Table II (Continued)
Short-Time Test Data

Steel No.	Brinell (R. T.)	Temperature of Test °F.	Ultimate Lbs. Per Sq. In.	Elongation % in 2 Inch	Reduction of Area	Ductility Factor
25—O-H Iron Copper-Molybdenum	92	1000	32,121	37.2	77.6	57.4
		1200	18,800	38.7	71.7	55.2
		1400	6,725	88.7	88.6	88.65
		1500	4,800	92.2	73.1	82.65
	Magnetic	1600*	7,375	21.5	20.2	20.85
		1700	6,280	24.5	24.2	24.35
26—18 Per Cent Chromium	156	1000	38,500	33.0	86.0	59.5
		1200	23,000	48.0	94.0	71.0
		1400	8,350	69.5	99.0	80.25
		1500	5,000	80.0	100.0	90.0
	Magnetic	1600	4,150	92.0	99.0	95.5
		1700	3,000	115.0	97.5	106.25

*Note increase in strength and decrease in ductility with change to gamma state.
Brinell—3000 Kg.—10 m.m. ball—room temperature.
Magnetic features determined on etched micro samples by means of a magnetic needle. Magnetic or nonmagnetic designates qualitative indication of presence or absence of ferrite in the materials at room temperature.

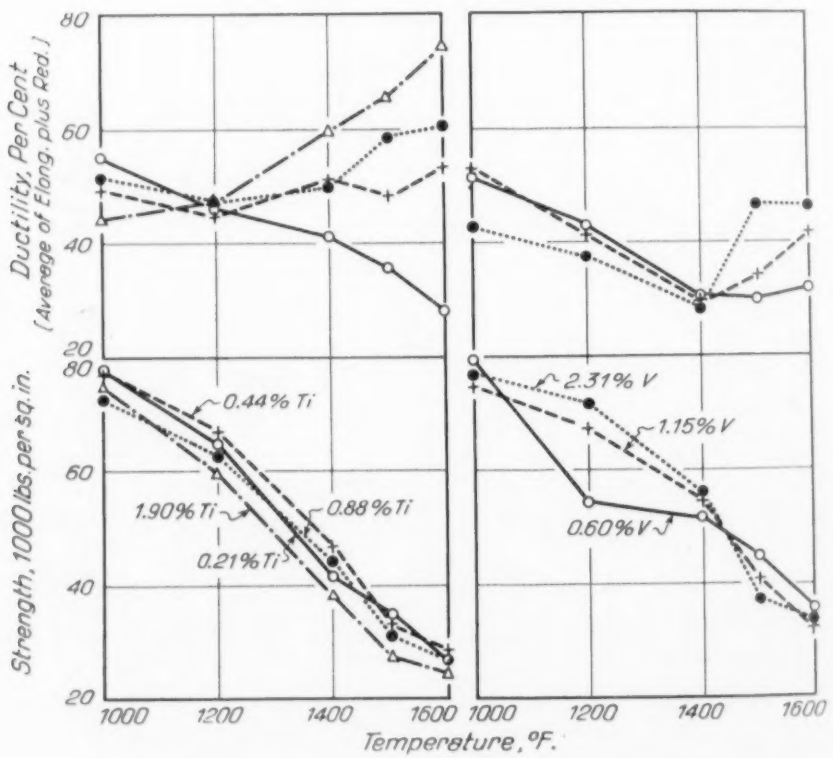

Fig. 1—(Left) Short-Time Properties of Titanium-Containing 18-8 Alloys.
Fig. 2—(Right) Short-Time Properties of Vanadium-Containing 18-8 Alloys.

a number of the alloys, including the titanium and vanadium containing alloys, are shown in Figs. 5, 6 and 7.

The silicon alloy, by virtue of its composition, was nonmagnetic and, consequently, free from ferrite at room temperature. It shows excellent ductility toward the high end of the temperature

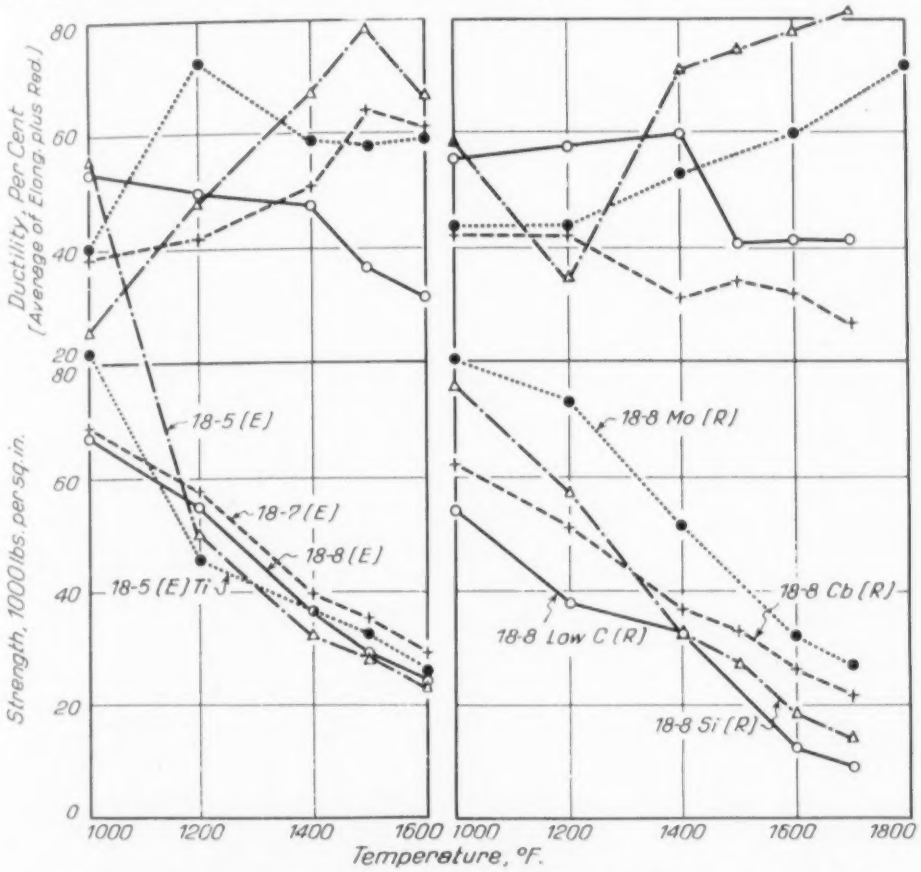

Fig. 3—(Left) Short-Time Properties of 18-8 (Experimental Steel 19) Compared with those Containing a Reduced Nickel Content.
Fig. 4—(Right) Short-Time Properties of Si, Mo and Cb-Containing 18-8 Alloys Compared with Commercially Rolled, Low Carbon 18-8.

range, but suffers a distinct drop in ductility at 1200 degrees Fahr. (650 degrees Cent.), which may be related to precipitation phenomenon occurring at this temperature. A check test from a different lot of bars of the alloy gave the same approximate result at 1200 degrees Fahr. (650 degrees Cent.).

Contrary to expectations, columbium did not act in a similar manner to titanium, as rather poor ductility was obtained in the presence of 1.10 per cent columbium.

Alteration of the chromium and nickel ratio, while maintaining

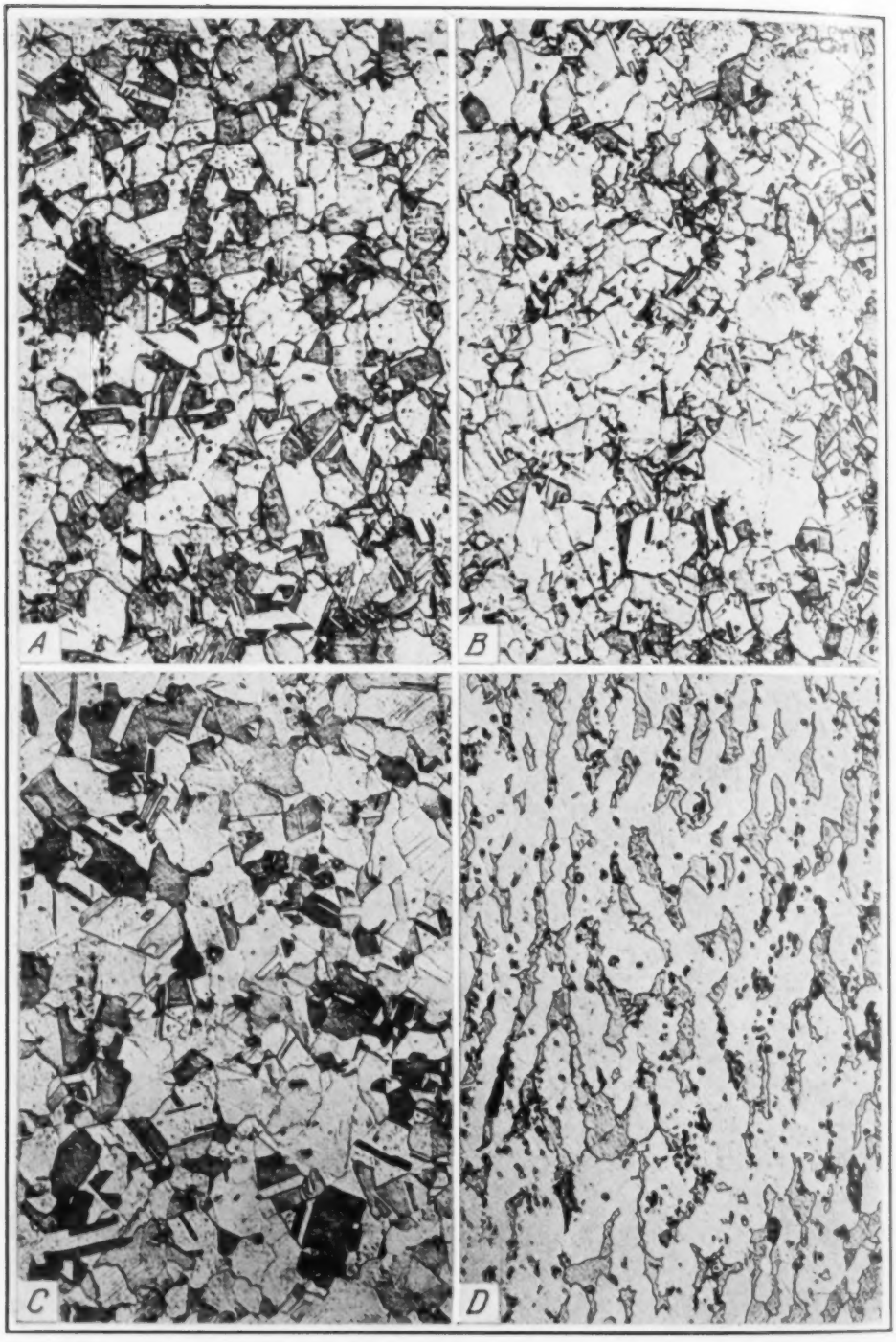

Fig. 5—Photomicrographs of Titanium-Containing 18-8 Alloys. A—0.21 Per Cent Titanium; B—0.44 Per Cent Titanium; C—0.88 Per Cent Titanium; D—1.90 Per Cent Titanium. Etched in Aqua Regia. × 200.

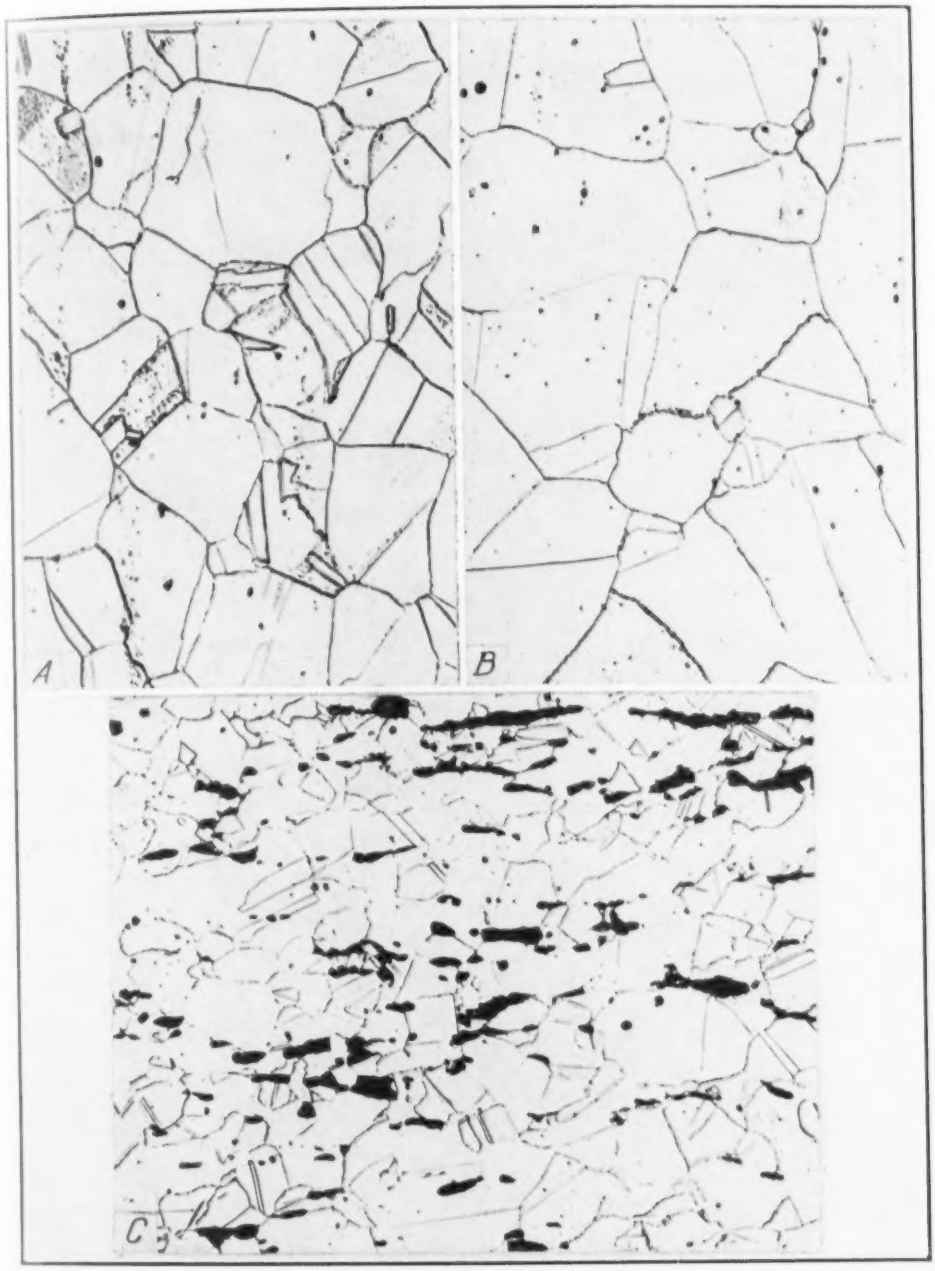

Fig. 6—Photomicrographs of Vanadium-Containing 18-8 Alloys. A—0.60 Per Cent Vanadium; B—1.15 Per Cent Vanadium; C—2.31 Per Cent Vanadium. Etched in Aqua Regia. × 200.

a purely austenitic structure, has no appreciable effect on high temperature ductility, as shown by the 18-14 and 22-12 alloys.

The effect of composition on the short-time strength at 1400 and 1600 degrees Fahr. (760-871 degrees Cent.) may be compared

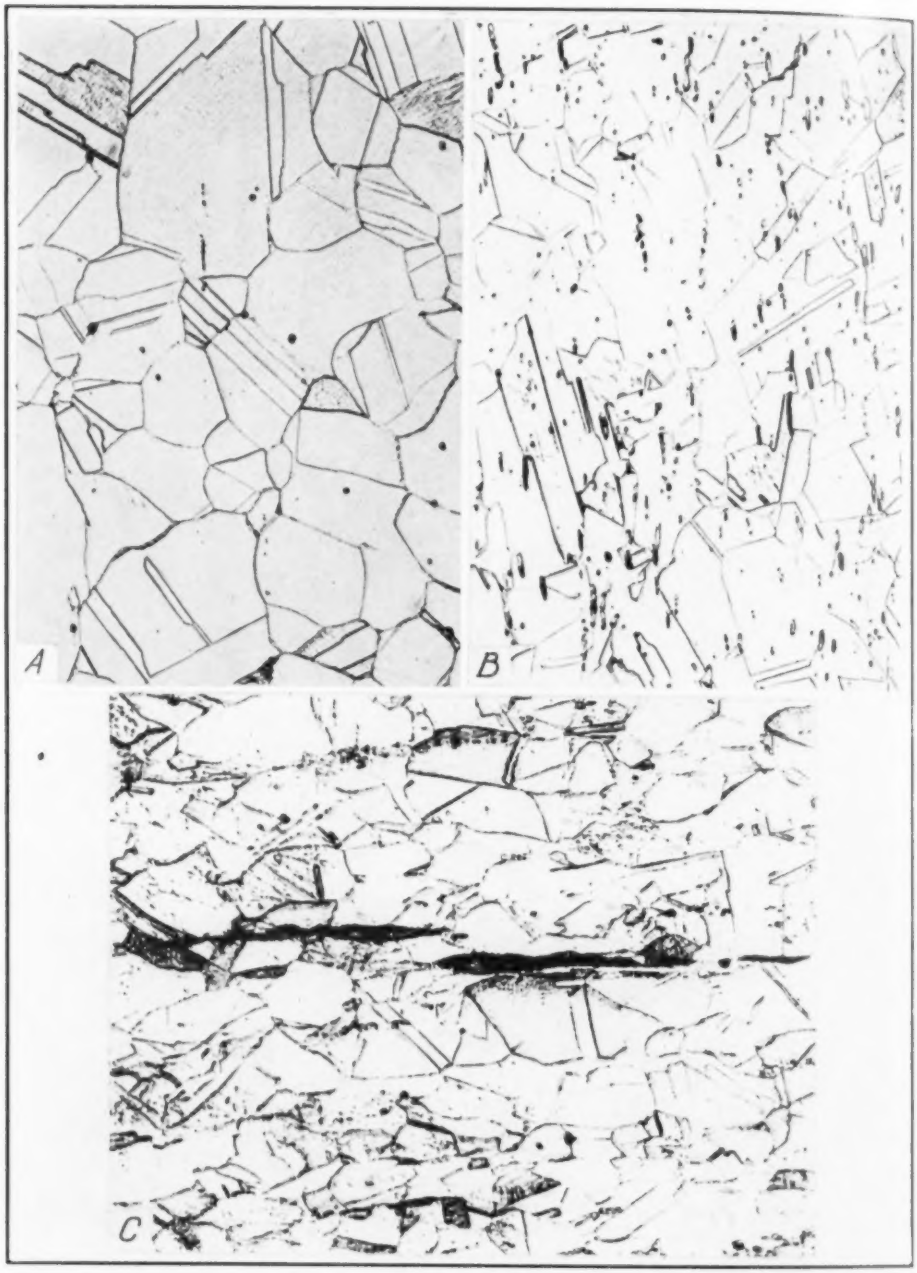

Fig. 7—Photomicrographs of 18-8 Alloys Containing: A—2.00 Per Cent Silicon; B—3.08 Per Cent Molybdenum; C—1.16 Per Cent Columbium. Etched in Aqua Regia. × 200.

from the values given in Table III. It will be noted that molybdenum and vanadium are quite effective in raising short-time strength values. Whether this increased strength is translated to long-time resistance to creep remains to be determined by tests now in progress.

Table III
Comparison of Short-Time Ultimate Strength at 1400 and 1600 Degrees Fahr.

Steel No.	Strength, Lbs. Per Sq. In. at 1400 Degrees Fahr.	at 1600 Degrees Fahr.
1—18-8 Low Carbon	32,750	13,650
2—18-8 High Carbon	30,900	16,190
3—18-8 Silicon	32,200	18,720
4—18-8 Molybdenum	51,420	32,450
5—18-8 Columbium	36,800	26,090
6—25-20 Chromium-Nickel	44,450	24,050
7—18-8 0.60 Per Cent Vanadium	51,900	35,350
8—18-8 1.15 Per Cent Vanadium	55,100	32,150
9—18-8 2.31 Per Cent Vanadium	55,600	33,400
10—18-8 0.21 Per Cent Titanium	41,150	26,700
11—18-8 0.44 Per Cent Titanium	46,350	28,150
12—18-8 0.88 Per Cent Titanium	44,750	26,700
13—18-8 1.90 Per Cent Titanium	38,100	24,850
14—18-14 Chromium-Nickel	34,950	.....
15—18-14 Titanium	35,000	23,900
16—21-12 Chromium-Nickel	38,250	25,000
17—21-12 Chromium-Nickel-Titanium	39,250	28,750
18—18-8	32,500	20,700
19—18-8 Titanium	36,750	24,400
20—18-7 Titanium	39,180	29,400
21—18-5 Titanium	36,500	26,450
22—18-5	32,290	22,600
23—18-8 Titanium	33,550	24,800
24—4-6% Chromium-Molybdenum	11,370	12,940
25—Open-Hearth Iron Copper-Molybdenum	6,725	7,375
26—18% Chromium	8,350	4,150

Discussion on Hot Ductility

Quoting Crawford and Worthington,[6] "Since the conception of creep has become recognized, the importance placed on tensile properties obtained in short-time elevated temperature tests has become less. The short-time test has a value, however. Ductility at high temperatures continues to carry significance as a measure of behavior in hot working processes—forging, riveting, billet piercing, hot-rolling—and such a test may be used to advantage in determining hot-short ranges."

The foregoing investigation was, therefore, conducted primarily to determine the intermediate temperature ductility of a group of austenitic steels, while tensile values were of secondary importance, if considered at all. With this thought in mind, the following discussion may be presented.

Under torsional deformation (twisting), Sauveur[7] states that ingot iron is more ductile at 500 degrees Cent. (930 degrees Fahr.)

[6]C. A. Crawford and R. Worthington, "Nickel and Nickel-Chromium Alloys Other Than the Nickel-Chromium-Iron Group." Symposium—Effect of Temperature on Metals, American Society for Testing Materials and American Society of Mechanical Engineers, 1931, p. 557.

[7]Albert Sauveur, "Steel at Elevated Temperatures," Transactions, American Society for Steel Treating, Vol. 17, 1930, p. 410.

than at 900 degrees Cent. (1650 degrees Fahr.), and that the hot-shortness apparent between 900 degrees Cent. (1650 degrees Fahr.) and 1000 degrees Cent. (1830 degrees Fahr.) appears to be strikingly related to the low ductility of gamma iron in this range of temperatures. Further, that when alpha iron transforms to gamma iron, at elevated temperatures, there is increased stiffness and decreased ductility and he infers from this that gamma iron is stronger and less ductile than alpha iron.

The short-time tests made on copper-molybdenum ingot iron and upon 5 per cent chromium, 0.5 per cent molybdenum steel confirm that the alpha state is more ductile than the gamma state. These materials show excellent ductility at temperatures below those corresponding to the gamma transformation and relatively poor ductility immediately above such temperatures. The alpha-delta steel containing 17.86 per cent chromium has only minor structural transformations which do not affect its ductility through the temperature range studied. High ductility is, therefore, retained in this alloy.

Hatfield[8] made short time tests of many materials, including numerous austenitic stainless steels at 800 degrees Cent. (1470 degrees Fahr.), and the results show generally less ductility (elongation and reduction of area) for the austenitic materials than those of alpha structure at the test temperatures. Similar low values for ductility were found by Jenkins and co-workers[9] on short-time tests of numerous austenitic alloys at 800 degrees Cent. (1470 degrees Fahr.). Data collected by Aborn and Bain[10] show that when failing in tension in short-time tests at elevated temperature, the wrought chromium-nickel iron alloys have reduced ductility in the intermediate range of temperatures corresponding approximately to the zone of carbide precipitation. Many other test data could be cited to show the lower ductility of face-centered crystalline materials, including Monel, nickel, Nichrome and many of the brasses at intermediate elevated temperatures, when compared to body centered alpha iron.

Variations in the high temperature ductility of austenites occur and may be influenced by such factors as composition, grain-size

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[8]Dr. W. H. Hatfield, "The Application of Science to the Steel Industry," Section V. TRANSACTIONS, American Society for Steel Treating, Vol. 16, 1929, p. 121.

[9]Jenkins, Tapsell, Austin and Rees, "Some Alloys for use at High Temperatures," *Journal*, Iron and Steel Institute, Vol. CXXI, No. 1, 1930, p. 237.

[10]Aborn and Bain, "The Wrought Austenitic Alloys," Symposium on Effect of Temperature on Metals, American Society for Testing Materials and American Society of Mechanical Engineers, 1931, p. 466.

and technique of deoxidation, also by testing conditions, i.e., rate of strain application. With regard to the last mentioned factor, Tapsell[11] mentions variation in short-time strength as being appreciably affected by rate of loading, but states that the final elongation and reduction of area at fracture do not vary appreciably for widely different commercial rates of testing even at high temperatures.

Grain size influences short-time ductility of austenitic 18-8, as previously shown by the author,[12] and the same holds true of straining, as applied in creep tests,[13] where a large-grained cast alloy showed much less total elongation than wrought metal of similar composition.

As to effect of state of deoxidation, data are available tending to show that the more oxidized the condition of the metal the less the hot ductility. Some recent work by N. Hamilton[14] correlates oxygen content and pierceability of alloy steels in the higher temperature ranges. At lower temperatures, ingot iron of low manganese content as contrasted to carbon steel containing normal manganese, exhibits wide differences in hot workability and ductility at approximately and slightly above the gamma transformation temperature. In metals of face-centered austenitic structure, such as nickel and Monel, there is a considerable difference in hot ductility from melt to melt, depending on deoxidation technique employed. Deformation tests, such as hot-bending of strip specimens, are conveniently used in practice to select material of good ductility for severe hot working operations extending down in to the temperature range of reduced ductility.

From physical tests performed on austenitic alloys at different temperatures, Schmidt and Jungwirth[15] conclude that hot-shortness is due to reversible changes taking place in the range 600-900 degrees Cent. (1110-1650 degrees Fahr.), and in tests made at 760 and 870 degrees Cent. (1400-1600 degrees Fahr.), the ductility increased sharply with increased breaking speed. They conclude that the precipitation phenomena causing hot shortness can be

[11]H. J. Tapsell, "Creep of Metals," Oxford University Press, 1931.

[12]loc. cit.

[13]Preliminary Report Joint High Temperature Committee.

[14]N. Hamilton, "Determination of Oxygen in Alloy Steels and Its Effect on Tube Piercing," T. P. 540, American Institute of Mining and Metallurgical Engineers, February 1934.

[15]Schmidt and Jungwirth, "Hot-shortness and Intercrystalline Corrosion of Austenitic Corrosion Resistant Steels," Korrosion U. Metallschutz, Vol. 9, 1933, p. 293-302.

suppressed by high initial temperatures and by quick deformation.

Based on work previously referred to, the author does not find himself in complete agreement with these conclusions, having found that high initial temperatures produce grain growth and exaggerated loss of ductility. Increased speed of testing within limits does, however, give apparently increased total elongation.

A recent and very interesting research was conducted by Krivobok[16] and co-workers, where a number of plain and specially modified austenitic alloys were tested under constant load at a specific temperature and the hours to break and per cent elongation* noted. The time to break varied with the alloy composition from a few hours to several hundred, test conditions being 8000 pounds per square inch stress at 1500 degrees Fahr. (815 degrees Cent.). Generally speaking, elongation of the alloys tested was comparatively low, even lower than test results reported herein. The test approximated an overloaded creep test with final elongation being taken after the test failed or was discontinued because of long life. Short-time tensile test values were also reported for a number of special alloys at 1500 degrees Fahr., and it is interesting to note that many alloys which may be suspected of containing ferrite, by reason of their composition, gave the highest ductility values.

It should not be inferred from the foregoing that ductility at the higher temperatures commonly used for working these austenitic alloys is improved by addition elements or by presence of ferrite. Generally, the simple, single phase austenites are more readily worked or rolled than complex ones. In the latter case, narrower temperature ranges and increased stiffness create difficulty in commercial production of many articles. Accordingly, the production of an austenitic steel of good intermediate temperature ductility, by creating a two-phase alloy containing some proportion of ferrite, is surrounded by many complex difficulties.

It is not the purpose of this paper to theorize on the reason for the lower ductility of gamma iron, either plain or with alloy content, as contrasted to alpha iron. Coincident with this, carbide precipitation has been accused of much ignoble action in chromium-nickel steels and may play some part in reducing their ductility within the precipitation range. From the observations recorded here, car-

[16]Krivobok, Smith and Lincoln. "Progress Report on Strength of Alloys at Elevated Temperature," Progress Report, Mining and Metallurgical Advisory Boards, Pittsburgh, Pa., 1933.

*Although not stated, the percentage elongation in Krivobok's work was assumed to be calculated on a 2-inch gage length.

bon does not seem to influence ductility to any great extent within the range 0.04 to 0.18 per cent carbon even though all tests were made within the precipitation range. This is true except insofar as reduction of carbon permits formation of ferrite. Again, referring to plain gamma iron as present in ingot iron, with all carbon supposedly in the dissolved state at the transformation temperature, the ductility is just as much impaired as with an 18-8 austenite containing 0.14 per cent or more carbon. In this particular case, it is known that oxygen causes a reduction of ductility producing hot-shortness.

The influence of stabilizing treatments toward ductility has not been studied except in a preliminary way and, consequently, is not reported in this investigation. In some cases slight improvement has been effected by stabilizing a long time (100 hours) at 1500 and 1650 degrees Fahr. (815-900 degrees Cent.) before testing, but in other cases little or no improvement occurs. The inference may be drawn that stabilizing, while producing minor changes in structure, does not change the characteristics of austenite sufficiently to appreciably improve hot ductility.

It seems quite apparent that the production of highly alloyed austenite with hot ductility equivalent to alpha-delta steels or to ordinary steels below their transformation points, is a difficult if not impossible task. Perhaps it would be well to recognize that austenitic steels are inherently different from ordinary steels and, as such, they must be handled and treated according to their specific properties. In many cases this is being done, but occasionally some slips occur or complaints are registered because the characteristics of the alloys are not known nor appreciated. In any event, ductility is adequate for many purposes, even though changes may be required in practices for working, rolling, forming or otherwise manufacturing into the desired form. It is believed other well known advantages more than offset the slight disadvantage of reduced ductility at certain temperatures.

Summary

Short-time tensile tests have been made on a series of commercial and experimental chromium-nickel austenitic steels within the temperature range wherein such steels exhibit reduced ductility under tensional deformation. Ingot iron, a pearlitic steel and an alpha-delta steel were included for comparative purposes.

The test procedure was alike for all specimens and, in consequence, gave comparative values for the ductility of each alloy. A "ductility factor" was assigned each test as an indication of ductility at that temperature.

Certain ambiguities exist in the action of the various addition agents, making it difficult to draw any sharply defined conclusions. The following generalizations have been made based on present data and numerous other data not reported herein.

Sauveur's statement that gamma iron is stronger and less ductile than alpha iron is readily confirmed. It is held that gamma iron is inherently less ductile than alpha iron at intermediate elevated temperatures.

There are apparently several factors affecting the ultimate ductility of chromium-nickel austenite which may be enumerated as follows:

(a) Formation of ferrite.
(b) Deoxidation effects produced by the addition element.
(c) Grain refinement produced by the addition element.
(d) Effect of addition element on carbide solubility and distribution (stabilization).

Addition elements tending to form ferrite show a tendency to improve hot ductility, but not to the same extent. Those elements having deoxidation power and grain refining action are more potent than those which simply form ferrite and stiffen the matrix. On the other hand, silicon promotes increased ductility at the higher temperatures in the absence of ferrite.

It has been shown that titanium increases ductility possibly first through deoxidation and grain refinement and finally through ferrite formation. A similar trend is shown for molybdenum and to a much lesser extent for vanadium. Columbium, in spite of its similar action to titanium in preventing intercrystalline corrosion effects, does not improve ductility. Conversely, reduction of nickel content, to the extent that ferrite is formed, improves ductility.

The production of a general purpose austenitic steel with intermediate elevated temperature ductility approaching that of alpha iron, seems improbable in the light of the foregoing investigation.

Acknowledgment

The author wishes to express his appreciation to the officials of The Babcock and Wilcox Tube Co. for permission to publish the

data contained in this paper. The helpful suggestions of N. Hamilton are acknowledged and special credit is deserved by C. P. Church and Z. Olzak for making the many elevated temperature tests. Thanks are also due to C. P. Church for preparation of the photomicrographs and to H. N. Austin for making the chemical determinations.

DISCUSSION

Written Discussion: By Russell Franks, Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y.

Mr. Newell deserves much credit for the large number of short-time high temperature tensile tests made at different temperatures in an effort to secure data relating to the ductility of the chromium-nickel steels when hot. As stated, the data presented pertain only to conditions involving short heating periods, such as those encountered in forging, hot rolling, riveting and billet piercing. It is further stated that lack of ductility has caused difficulty in certain fabricating operations such as tube bending and expanding or plate bending. A study of the paper leads to the belief that it would have been well had additional tests been made on typical steels at higher temperatures, because usually initial temperatures above 1700 degrees Fahr. (925 degrees Cent.) are employed for these operations. If this had been done temperature ranges giving the best results for both types of operation might have been established. The importance of such data, as well as those designed to show the ranges in which brittleness occurs, can hardly be questioned.

It is generally accepted that ductility at high temperatures does carry significance as a measure of the behavior of a steel in hot working processes. However, is it not true that the strength of a given material also affects its ability to be hot-worked? It is difficult to agree with Mr. Newell's statement which reveals that in the results obtained, only the ductility values were seriously considered, whereas the tensile values were of secondary importance, if considered at all. According to the ductility values given in Table II of the paper, steel #18 containing 17.92 per cent chromium, 9.14 per cent nickel, 0.51 per cent silicon, 0.33 per cent manganese and 0.092 per cent carbon should be slightly more difficult to hot pierce than steel #6, which contains 24.96 per cent chromium, 21.00 per cent nickel, 0.97 per cent silicon, 0.52 per cent manganese and 0.10 per cent carbon. The ductility values also indicate somewhat superior hot rolling and fabricating properties for the higher chromium and nickel steel, and it is my impression that under present conditions in the majority of commercial mills the reverse is actually true.

Mr. Newell states that heating the chromium-nickel steels in the carbide precipitation range may cause a reduction of impact strength, but ordinarily the impact strength remaining in low carbon steels is substantial. Although this is the case, the values so obtained should not be considered lightly. Usually under service conditions a corrosive influence is present and the tendency to develop brittleness is more pronounced. The importance of this cannot be overlooked in selecting a steel for high temperature service. For example, the brittleness exhibited by the plain 18 per cent chromium steel at room tempera-

ture after use at elevated temperatures resulted in the replacement of this steel with the 18 per cent chromium-8 per cent nickel steel for oil cracking tube service, even though at elevated temperature the plain chromium steel possessed appreciable ductility. Of course, it is realized that Mr. Newell's experiments were not intended to cover all phases of high temperature service. However, the foregoing facts seem pertinent in view of certain of the data recorded in the present paper.

The conclusions concerning the effect of the various addition agents on the ductility of the austenitic chromium-nickel steels at high temperatures should be commented upon. It is concluded that titanium improves the ductility of the steels at elevated temperatures, while columbium impairs this property. We should like to submit the results of Izod impact tests conducted at our laboratories on steels with and without titanium and columbium.

Results of Izod Impact Tests at Room Temperature

Per Cent								Impact Value
Cr	Ni	Si	Mn	C	Ti	Cb	Condition of Steel	Ft. Lb.
18.45	8.56	0.23	0.47	0.12	....	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.)	120
18.45	8.56	0.23	0.47	0.12	....	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.) Held one month at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	46
18.58	8.68	0.42	0.55	0.10	0.38	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.)	111
18.58	8.68	0.42	0.55	0.10	0.38	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.) Held one month at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	82
18.01	9.08	0.46	0.63	0.12	0.94	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.)	101
18.01	9.08	0.46	0.63	0.12	0.94	....	Quenched from 1150 degrees Cent. (2100 degrees Fahr.) Held one month at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	20
18.04	8.86	0.42	0.54	0.092	....	0.75	Quenched from 1150 degrees Cent. (2100 degrees Fahr.)	120
18.04	8.86	0.42	0.54	0.092	....	0.75	Quenched from 1150 degrees Cent. (2100 degrees Fahr.) Held one month at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	95
18.38	8.97	0.63	0.68	0.10	....	1.16	Quenched from 1150 degrees Cent. (2100 degrees Fahr.)	104
18.38	8.97	0.63	0.68	0.10	....	1.16	Quenched from 1150 degrees Cent. (2100 degrees Fahr.) Held one month at 750 degrees Cent. (1380 degrees Fahr.) and air-cooled.	40

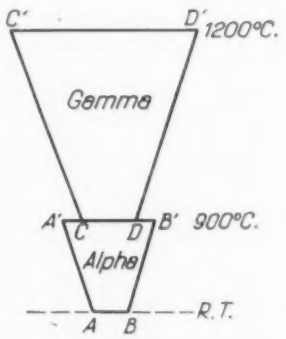
These reveal that after holding for relatively long periods at 750 degrees Cent. (1380 degrees Fahr.) the toughness of a steel containing 18.58 per cent chromium and 8.68 per cent nickel with 0.10 per cent carbon and 0.38 per cent titanium remains for practical purposes almost unimpaired, whereas a similar steel containing 0.12 per cent carbon and 0.94 per cent titanium decreases appreciably in impact strength. It is generally understood that in steels of this type about four times as much titanium as carbon is needed to fix the carbon present, and these results indicate that the large excess of titanium alloyed with the solid solution of iron-chromium-nickel detrimentally affects stability at

high temperature. Approximately seven times as much columbium as carbon is required to combine with the carbon in these steels, and again it is shown that the excess of the carbide-forming element reduces the stability of the iron-chromium-nickel matrix at elevated temperatures. On the other hand, the results given by Mr. Newell show that the 18-8 steel with the highest titanium content (1.90 per cent titanium) is the most ductile at elevated temperatures, a condition indicating that this metal will probably be more suitable than one containing less titanium. It is unfortunate that Mr. Newell did not include in his tests a steel of somewhat lower columbium content.

It is interesting to note in Mr. Newell's results that the low carbon 18-8 steels performed well in relation to the other types tested. My belief is that in suitable applications much is to be gained by using these steels. It is to be hoped that Mr. Newell will continue his valuable work in an effort to secure constructive data concerning the most advantageous temperatures to be employed in hot working the austenitic chromium-nickel steels.

Written Discussion: By Dr. Albert Sauveur, Harvard University, Cambridge, Mass.

Mr. Newell quotes me correctly when he reports that from the results of some twisting tests at elevated temperatures, I concluded that the alpha-gamma transformation was accompanied by decreased ductility and increased strength; that is, alpha iron immediately before it is converted into gamma iron and over a certain range of temperature below its allotropic transformation is *more* ductile than gamma immediately upon forming and even more ductile than gamma iron at temperatures somewhat exceeding the critical temperature. To state, however, that gamma iron is stronger and less ductile than alpha iron without suitable qualification is somewhat misleading. I am in the habit of describing the phenomenon by means of a simple diagram.



Let AB represent the ductility of alpha iron at room temperature. Its ductility increases with increasing temperature—except for a temporary decrease in the blue heat range. It is maximum at the highest temperature at which it can exist; that is, immediately before it is converted in gamma iron at about 900 degrees Cent. (1650 degrees Fahr.). It is represented in a diagram by the distance A′B′ > AB. The allotropic transformation is accompanied by a loss of ductility, its new phase, gamma iron having a ductility represented by the distance CD < A′B′. In other words, A′B′ represents the ductility of

alpha iron (necessarily maximum) at the highest temperature at which alpha iron can exist, while CD represents the ductility of gamma iron (necessarily minimum) at the lowest temperatures at which gamma iron can exist. Increasing the temperature of gamma iron results in increased ductility—until it becomes greater than the maximum ductility of alpha iron—at 1200 degrees Cent. (2190 degrees Fahr.) it might be represented by the C′D′ very much greater than A′B′. I have expressed the belief that the red shortness of iron is confined to that range of temperature where gamma iron has relatively little ductility, namely between 900 and 1000 degrees Cent. (1650-1830 degrees Fahr.), and that alpha iron is never red short.

Written Discussion: By R. H. Aborn, U. S. Steel Corp., Research Laboratory, Kearny, N. J.

In view of the author's statement, on page 227, that the as-forged or rolled condition is conducive to highest ductility in short-time elevated temperature tests it may be of interest to note certain results obtained in this laboratory on alloys of comparable composition, but tested in the annealed (or annealed-stabilized) condition. The following table provides a comparison.

	BHN (original)	Ductility Factor at 1000 Degrees Fahr.	Ductility Factor at 1200 Degrees Fahr.	Ductility Factor at 1500 Degrees Fahr.
Low-Carbon 18-8 annealed	165	46.7	46.2	48.4
Author's corresponding Alloy (#1) as forged	143	55.5	57.9	46.2*
Stabilized (Ti-bearing) 18-8	155	49.9	56.9	71.4
Author's corresponding Alloy (#12) as forged	175	51.7	47.1	58.8
22-12 Chromium-Nickel annealed	175	45.3	49.4	71.8
Author's corresponding Alloy (#16) as forged	169	51.6	47.3	41.4
Stabilized 22-12 Chromium-Nickel	165	30.6	42.9	75.4
Author's corresponding Alloy (#17) as forged	179	47.5	41.4	41.5
Molybdenum-bearing 18-8 annealed	149	46.0	55.1	57.4
Author's corresponding Alloy (#4) as forged	207	43.7	44.2	56.8**

* Direct value from author's paper, TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1931, p. 673.

** Interpolated value.

It will be seen that more than half of the ductility factors are higher in the annealed than in the as-forged condition (author's standard); this trend is particularly evident at testing temperatures above 1000 degrees Fahr. (540 degrees Cent.). While the author's statement may be true with respect to the behavior of the regular 18-8 grade, it appears that any generalization extending to other austenitic chromium-nickel steels is open to some doubt.

Author's Closure

The author wishes to thank Mr. Franks for his interesting discussion.

The paper was primarily intended to throw light on those temperature ranges where hot-shortness appears in straining during certain forming operations where the work-piece cannot be maintained at the optimum temperature for working the alloy. Also, to point out that tubes of austenitic chromium-nickel steels, when failing under pressure on overheating, will do so with an abrupt fracture and that this is characteristic of not only 18-8 but other austenitic chromium-nickel combinations. Additional tests, such as suggested by Mr. Franks, have been made on several of the alloys at temperatures extending much higher than those reported. In many cases, the shortness dis-

appears to a great extent within the ranges used for piercing, rolling, or forging, otherwise, it would be impossible to produce the alloys in commercial forms.

Strength undoubtedly affects ability to be hot-worked, the higher strength steels requiring more power and more numerous passes in effecting a given reduction in cross section than is the case with the lower strength alloys.

It is well known that steel No. 18, containing 17.92 per cent chromium, 9.14 per cent nickel and 0.092 per cent carbon is much easier to pierce than steel No. 6, which contains 24.96 per cent chromium, 21 per cent nickel, and 0.10 per cent carbon. Although ductility values are about equal for the alloys at intermediate elevated temperatures, the reverse is true in the usual working ranges for piercing and rolling as may be seen from the following data:

No. 6
Chromium 25 Per Cent—Nickel 21 Per Cent

Degrees Fahr.	Ultimate Strength p.s.i.	Elongation % in 2 inches	Reduction %
2000	7000	62.5	49.6
2100	4860	62.0	45.8
2200	3650	70.0	54.7
2300	2900	92.5	66.5

No. 18
Chromium 18 Per Cent—Nickel 8 Per Cent

2000	4700	85.0	74.0
2100	3575	82.8	80.5
2200	2500	100.0	100.0
2300	2300	122.5	99.8

The results submitted by Mr. Franks pertaining to dynamic impact properties of alloys at room temperature are of interest and may be considered satisfactory in all cases except for the 0.94 per cent titanium alloy which dropped to 20 ft.-lbs. on long treating. Being only concerned with static tensile properties, in the present investigation, no tests were made as to impact properties but as Mr. Franks knows, only low carbon alloys are used in high temperature applications where shock is likely to be encountered after cooling. The low carbon alloys remain tough and shock-resistant.

It was not meant to infer that 1.90 per cent titanium is more suitable than one containing less titanium but only to show that sufficient quantities of a delta-forming element tend to improve ductile properties by formation of an austenite-ferrite duplex structure. In selecting the optimum amount of the addition element to use, considerations other than ductility also influence the problem, last but not least of which is economy. As to columbium, possibly the opportunity will present itself to test other alloys containing this element.

The author concurs with Mr. Franks that low carbon "18-8" steels performed well in relation to other types tested and experience has already shown that much is to be gained by suitable application of these steels.

Professor Sauveur's simple diagram ably depicts the relationship between the ductility of alpha iron and gamma iron at various temperatures in those steels having allotropic transformations. In the straight gamma iron alloys, having no or only minor transformations, the hot short range is somewhat wider than in the transformable alloys and lessened ductility may be in evidence between 1250 and 1850 degrees Fahr., or higher. At ordinary temperature, the gamma alloys may be highly ductile and also quite ductile at high

temperatures although stiff due to their high alloy content. In the intermediate range, their ductility never approaches that of alpha iron at the highest temperature at which it can exist.

In view of the ductility of alpha iron just before its transformation, it is rational to expect that the presence of some alpha iron in the gamma type alloys would improve the ductility of these alloys at intermediate temperatures. The evidence would seem to indicate that this is the case.

Dr. Aborn's interesting discussion would indicate that further work on annealing for carbide fixation should be done to accurately determine whether or not improvement in ductility would be gained thereby. In a few tests along this line, the author found a very slight improvement in ductilty in plain "18-8" alloys as a result of annealing with the major change being a shifting of the temperature of minimum ductility. In the silicon-containing alloys, no substantial improvement in ductility factor was obtained over the "as-rolled" condition when the alloy had been stabilized, viz. Analysis: carbon 0.14 per cent, manganese 0.55 per cent, silicon 2.00 per cent, chromium 17.54 per cent, nickel 9.80 per cent.

Temperature	As-Rolled	Stabilized 100 Hours at 1575 Degrees Fahr.
1400°	71.35	79.45
1500°	75.0	64.55
1600°	78.6	75.9
1700°	82.1	85.6

The statement on page 227 that the grain-size affects elevated temperature ductility is correct regardless of composition when related to gamma iron alloys. However, it was meant to imply that the fine-grained forged or as-rolled condition provides greater ductility than any annealing treatment which might cause an enlargement of the grain of the metal.

The author thanks those who offered discussion for enhancing the value of the paper.

THE COBALT-MOLYBDENUM SYSTEM

By W. P. Sykes and Howard F. Graff

Abstract

The constitutional diagram of this binary system has been constructed from data derived from microstructures, X-ray photograms, thermal analysis and measurements of electrical resistance and thermal expansion.

Cobalt dissolves about 26 per cent of molybdenum in the solid at 1360 degrees Cent., the eutectic temperature. The solid solubility of molybdenum in cobalt decreases to less than 2 per cent at 700 degrees Cent. The complete eutectic occurs at a composition near 36.5 per cent molybdenum and is made up of the hexagonal cobalt-rich solid solution, γ and ϵ, an intermediate phase corresponding to the fomula CoMo. This ϵ phase is formed from the melt upon cooling, by a peritectic reaction at 1550 degrees Cent. between the cobalt-rich liquid and a second intermetallic phase, η, containing about 71 per cent molybdenum and represented by the formula Co_2Mo_3.

The η phase forms at 1620 degrees Cent. upon cooling from the melt by a second peritectic reaction between the cobalt-rich liquid and the molybednum-rich δ phase. η decomposes at 1250 degrees Cent. upon cooling into ϵ and δ.

The δ phase represents the molybdenum-rich solid solution dissolving about 3 per cent cobalt at 1600 degrees Cent. (2910 degrees Fahr.)

The face-centered cubic form of cobalt extends to a molybdenum concentration of some 25 per cent at about 1310 degrees Cent. At this temperature it is formed as the β phase upon cooling the hexagonal solid solution, by the reaction $\gamma + \epsilon \rightleftarrows \beta$. At 1200 degrees Cent. another hexagonal phase, Θ, containing about 25 per cent molybdenum forms upon cooling by the reaction $\beta + \epsilon \rightleftarrows \Theta$. This phase is stable between 1200 degrees Cent. and 1050 degrees Cent. At the latter temperature Θ decomposes by a reaction which at present is somewhat obscure, but below 1000 degrees the structure is represented by β and another phase, K, containing about 32 per cent molybdenum.

The higher transformation point in cobalt (1020 de-

A paper presented before the Sixteenth Annual Convention of the Society held in New York City, October 1 to 5, 1934. Of the authors W. P. Sykes is metallurgist, and H. F. Graff is assistant metallurgist, Cleveland Wire Works, General Electric Co., Cleveland, Ohio. Manuscript received July 3, 1934.

grees Cent.) appears to be raised to about 1310 degrees by the addition of 25 per cent molybdenum, while the lower point (420 degrees Cent.) is depressed to about 240 degrees Cent. at a molybdenum concentration of 1 to 2 per cent.

The cobalt-rich solid solution, β, is subject to age hardening at temperatures above 450 degrees Cent. A maximum hardness of Rockwell C 63 was developed in an alloy of cobalt + 15 per cent molydenum by aging at 550 degrees Cent. for 100 hours. The hardness developed by aging in these alloys approximates that of the cobalt-tungsten alloys but is less resistant to protracted heating at temperatures in the range of 600 to 700 degrees Cent.

THE study of this system was undertaken primarily to observe the physical properties and especially the hardness characteristics of the terminal solid solutions. For a satisfactory understanding of these phases a detailed survey of the entire system seemed desirable in view of the conflicting interpretations of earlier data.

Previous Investigations

This system has been described in part by Raydt and Tammann, (1)* by Takeshi Takei (2) and most recently by Köster and Tonn (3). The last named investigators offered a constitutional diagram based upon magnetic and dilatometric analyses as well as microstructures and include some data relating to age hardening and magnetic properties in the cobalt-rich solid solutions. The conclusions drawn by these investigators will be discussed later in connection with the constitutional diagram.

Raydt and Tammann confined their investigation mainly to the solidus-liquidus temperature range. Their diagram shows the eutectic range extending from 28 to 62 per cent molybdenum, the eutectic composition at 37 per cent molybdenum and the melting point of the eutectic at 1330 degrees Cent. (2425 degrees Fahr.). The intermetallic phase CoMo is shown as forming at 1485 degrees Cent. (2705 degrees Fahr.) by a peritectic reaction between molybdenum and the cobalt rich liquid.

The following abstract of Takei's report includes his findings and his interpretation. "The equilibrium diagram of the cobalt-molybdenum system has been studied by means of the dilatometric

*The figures appearing in parentheses refer to the bibliography appended to this paper.

method, magnetic analysis and microscopic examination. With an increasing amount of molybdenum the transformation point of pure cobalt (472 degrees Cent.) is gradually raised on heating and lowered on cooling, reaching room temperature at about 13 per cent molybdenum. When the molybdenum content reaches 22 per cent the above transformation becomes reversible in both heating and cooling, and when the molybdenum content is further increased and

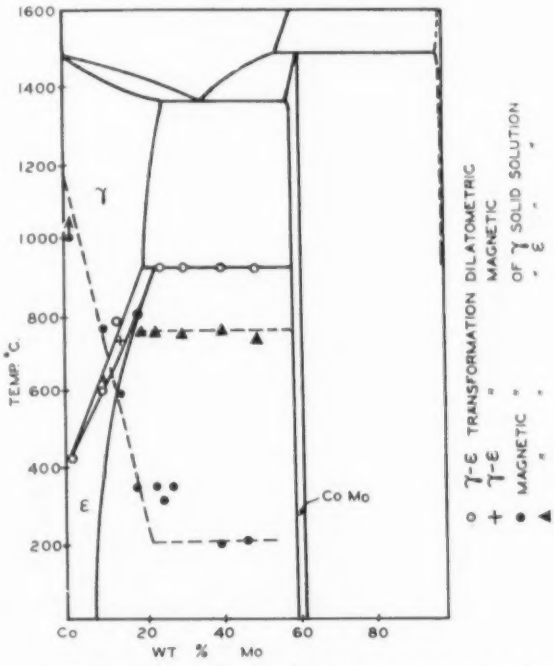


Fig. 1—Constitutional Diagram of Cobalt-Molybdenum System after Köster and Tonn.

enters the range between 27 and 55 per cent the alloy undergoes a peritectoid reaction (gamma + epsilon $\rightleftarrows$ hexagonal) at 1040 degrees Cent. (1905 degrees Fahr.). (The gamma phase here mentioned refers to the face-centered cubic modification of cobalt). The alloys between 58 and 71 per cent and those between 62 and 96 per cent molybdenum form two solid solutions, epsilon and eta, as a result of the peritectic reactions, liquid + eta $\rightleftarrows$ epsilon at about 1500 degrees Cent. (2730 degrees Fahr.) and liquid + delta (molybdenum) $\rightleftarrows$ eta at 1550 degrees Cent. (2820 degrees Fahr.) respectively. The two solid solutions are mainly composed of CoMo and Co_2Mo_3. The epsilon phase produces an eutectic with the gamma solid solution, while the eta phase decomposes into the epsilon and delta solid solutions at 1340 degrees Cent. (2445 degrees

Fahr.). The delta solid solution dissolves about 2 per cent of cobalt."

The diagram of Köster and Tonn is reproduced in Fig. 1. As will be noted this diagram in the cobalt-rich field has the form suggested by Takei although the magnetic data are rather difficult of interpretation. No indication of the intermediate phase at 71 per cent molybdenum is shown in this case. Moreover these investigators

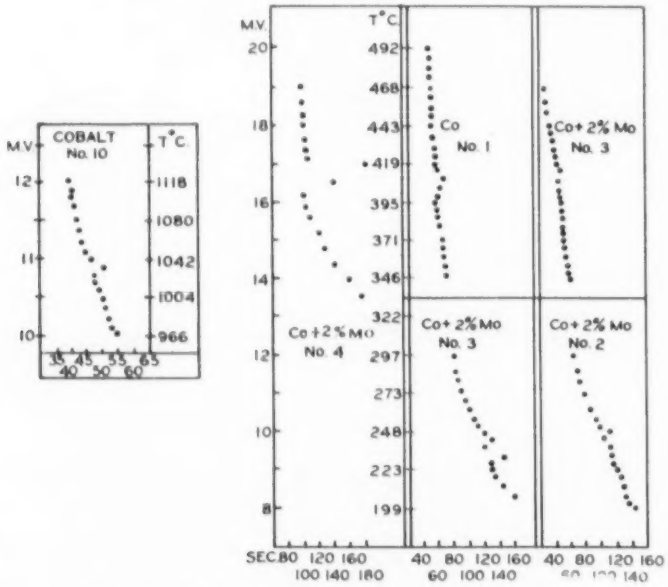


Fig. 2—Cooling Curves. Cobalt and Cobalt-Molybdenum Alloys.

consider the upper transformation point in pure cobalt as merely a Curie point involving no change in lattice. Takei apparently makes no mention of this point. Köster and Tonn from dilatometric data conclude that the lower transformation is raised by the addition of molybdenum, although they include no history of the specimens used in these measurements. As will be noted later the previous treatment of the cobalt-rich solid solutions must be considered in the interpretation of any expansion measurements made in this range of temperatures.

Materials and Methods

Both the cobalt and molybdenum metals used in this work were in the form of hydrogen-reduced powder prepared by methods previously described (4), (5). The cobalt contained about 1 per cent impurities including 0.6 per cent nickel and 0.2 per cent iron. The

purity of the molybdenum was about 99.8 per cent. Alloys were prepared from briquettes of the mixed powders either by sintering, by melting in alundum crucibles or by a combination of both methods. All heatings at elevated temperatures were carried out in the hydrogen atmosphere of a tungsten-wound alundum muffle resistor furnace with rheostat control. In order to maintain a constant temperature during long treating periods one such furnace was equipped with a voltage regulator operated by an automatic voltage control. The hydrogen flow was held nearly constant by a reduction valve in the supply line. By these means it was possible to operate the furnace at any desired temperature between 1000 and 1600 degrees Cent. (1830-2910 degrees Fahr.) with a maximum variation of one per cent over periods of days. Temperatures above 1300 degrees Cent. (2370 degrees Fahr.) were measured with an optical pyrometer which had been recently calibrated by observations on the melting points of nickel and iron melted in the hydrogen atmosphere. For freezing point determinations and the detection of critical points a rare metal couple was used in conjunction with a potentiometer and galvanometer.

Thermal Data on Transformation Points in Cobalt

In an earlier paper (4) the critical points in cobalt were placed at approximately 420 and 1020 degrees Cent. (790-1870 degrees Fahr.) mainly from evidence obtained by X-ray diffraction methods. The marked halt in the cooling curve of cobalt at the lower temperature was also mentioned. In connection with the present investigation further attempts were made to detect some evidence of the upper critical point by thermal analysis and especially to determine the effect of molybdenum upon the lower point.

The data reported here were obtained from 50-gram melts of cobalt or the cobalt-molybdenum alloys fused in alundum crucibles in the hydrogen atmosphere of a vertical tungsten wound furnace. The cooling was observed with a galvanometer and rare metal couple in a silica protection tube. In the lower ranges of temperature a chromel-alumel couple was substituted for the rare metal couple.

In several instances a barely detectable halt was observed at temperatures between 1000 and 1050 degrees Cent. (1830-1920 degrees Fahr.) while cooling cobalt from the freezing temperature. These halts were never noticed in metal which had been once cooled below

1000 degrees Cent. (1830 degrees Fahr.) and then reheated for some time between 1200 and 1400 degrees Cent. (2190-2550 degrees Fahr.).

One such set of data is shown in Fig. 2 marked cobalt No. 10. The cooling rate in this case, between 1200 and 1000 degrees Cent. (2190-1830 degrees Fahr.) was from 5 to 8 degrees Cent. per minute. The halt at about 420 degrees Cent. (790 degrees Fahr.) was pronounced in all cases. The intensity of this halt appeared to be greatest after the metal had been held for some hours at a temperature of 600 to 800 degrees Cent. (1110-1470 degrees Fahr.). Such a cooling curve is shown in Fig. 2 marked cobalt No. 4.

No indication of either thermal point was observed in an alloy of cobalt with 5 per cent molybdenum cooled from 1400 to 100 degrees Cent. (2550-210 degrees Fahr.). An alloy of 2 per cent molybdenum, however, gave evidence of a slight heat evolution just below 420 degrees Cent. (790 degrees Fahr.) during the initial cooling from the melt. This is represented as Co + 2 per cent Mo (No. 1) in Fig. 2. This specimen was reheated immediately to about 400 degrees Cent. (750 degrees Fahr.) and held at 400 ± 15 degrees Cent. for 50 hours. Upon subsequent cooling the discontinuity shown in curve No. 2 was observed at about 250 degrees Cent. (480 degrees Fahr.).

Since by resistance measurements the solid solubility of molybdenum in cobalt had been indicated as below 2 per cent at 700 degrees Cent. (1290 degrees Fahr.) it appeared that a longer heating at about 500 degrees Cent. (930 degrees Fahr.) might bring the alloy more nearly to a state of structural equilibrium. The two curves marked No. 3 in Fig. 2 resulted upon cooling this specimen after holding at 500 degrees Cent. (930 degrees Fahr.) for 50 hours. There is still a suggestion of the point which occurs in pure cobalt at 420 degrees Cent. (790 degrees Fahr.) together with a seemingly double cusp between 240 and 230 degrees Cent. (465-445 degrees Fahr.). These data indicate the effect of molybdenum in depressing the lower critical point of cobalt and together with the dilatometric results have been embodied in the constitutional diagram as shown in Fig. 7.

Dilatometric Data

To obtain further possible information on the nature of the cobalt-molybdenum alloys in the region of the lower critical point,

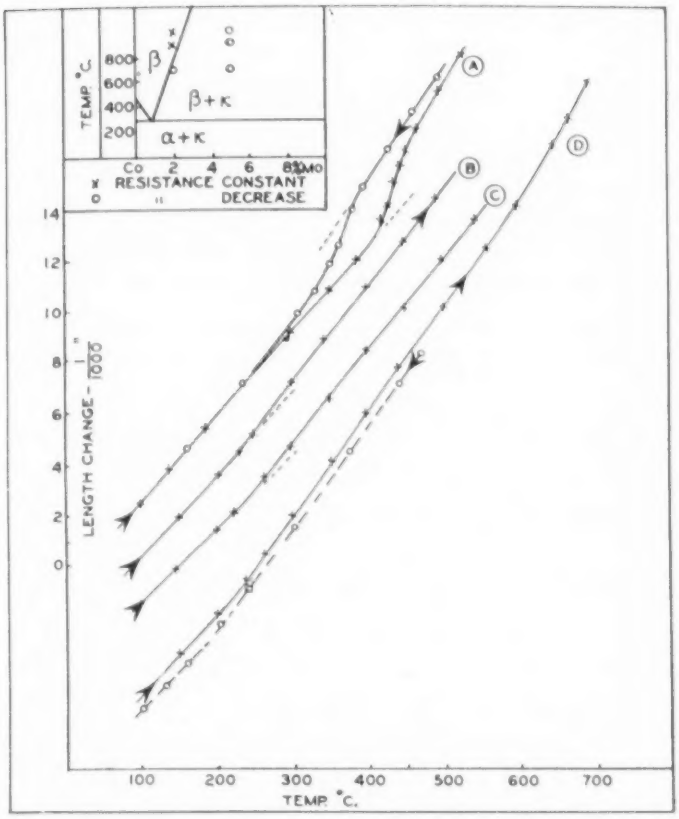


Fig. 3—Expansion Curves of Cobalt and Cobalt-Molybdenum Alloys. A—Cobalt; B—Cobalt, 2 Per Cent Molybdenum; C—Cobalt, 5 Per Cent Molybdenum. Specimens A, B, and C Previously Cooled from 800 to 300 Degrees Cent. in 100 Hours. D—Cobalt, 5 Per Cent Molybdenum Previously Heated at 1000 Degrees Cent. for 25 Hours and Quenched.

thermal expansion measurements were made on cobalt and two alloys of 2 and 5 per cent molybdenum respectively.

The equipment used for these determinations was similar in construction to that described by Scott (6) and by Kempf (7). The quartz tube was supported in the lower end of a nichrome-wound furnace with rheostat control. Specimens 3 inches in length and 5/8 inches in diameter were machined from cast alloys which had been heated in hydrogen for 50 hours at 1300 degrees Cent. after solidification. A chromel-alumel couple wedged into a drilled hole in the middle of the specimen served to indicate the temperature in conjunction with a potentiometer and galvanometer. The heating rate was maintained nearly constant between one and two degrees Cent. per minute, though in cooling below 200 degrees Cent. (390 degrees Fahr.) the rate decreased somewhat. In order to approach as nearly as pos-

sible structural equilibrium, the specimens, after machining, were reheated to 800 degrees Cent. (1470 degrees Fahr.) and cooled to about 300 degrees Cent. (570 degrees Fahr.) over a period of 100 hours.

In Fig. 3 curves A show the course of the thermal expansion and contraction of the cobalt specimen. The first change in slope of the expansion curve occurs at about 420 degrees Cent. (790 degrees Fahr.) and in the contraction curve at about 380 degrees Cent. (715 degrees Fahr.). The expansion curves of the alloys show a change in slope at 230-240 degrees Cent. (445-465 degrees Fahr.). For reasons of clarity the contraction curves of the alloys are not shown here. In general they coincide closely with the expansion curves. Changes in resistance and hardness resulting from low temperature treatments indicate that structural changes occur very slowly at 400 degrees Cent. (750 degrees Fahr.) in the cobalt-rich solid solutions of molybdenum or tungsten. To observe the expansion characteristics of a supersaturated solid solution the 5 per cent molybdenum alloy was reheated at 1000 degrees Cent. (1830 degrees Fahr.) for 25 hours and quenched. Subsequent measurements of thermal expansion resulted in curve D of Fig. 3 which appears to change in slope first at about 225 degrees Cent. At about 600 degrees Cent. (1110 degrees Fahr.) the slope again distinctly increases. After cooling this alloy to 100 degrees Cent. a marked decrease in length was observed as indicated by the lower curve of D. Apparently some precipitation of the molybdenum-rich phase had taken place at the higher temperatures during the measurements, which would result in a volume decrease in the specimen.

In the upper corner of Fig. 3 is inserted a plan of the constitutional diagram in the low temperature, cobalt-rich field. This is suggested by the combined data from the measurements of resistance and of thermal expansion and the cooling curves.

Dilatometric data recently obtained from alloys of cobalt and tungsten are of such striking similarity as to warrant inclusion here. These are shown in Fig. 4 together with the history of the specimens.

The expansion curves of the supersaturated solid solution (alloys quenched from elevated temperatures) differ markedly from those of the alloys which had been treated to approximate structural equilibrium at 300 or 400 degrees Cent. (570-750 degrees Fahr.). No explanation of the form of these curves will be offered. It should suffice, however, to emphasize the important effect of previous

treatment upon the behavior of the specimen used for expansion measurements.

Electrical Resistance

For the purpose of determining the solid solubility of molybdenum in cobalt between 700 and 1000 degrees Cent. (1290-2010 degrees Fahr.) measurements of electrical resistance were made on a

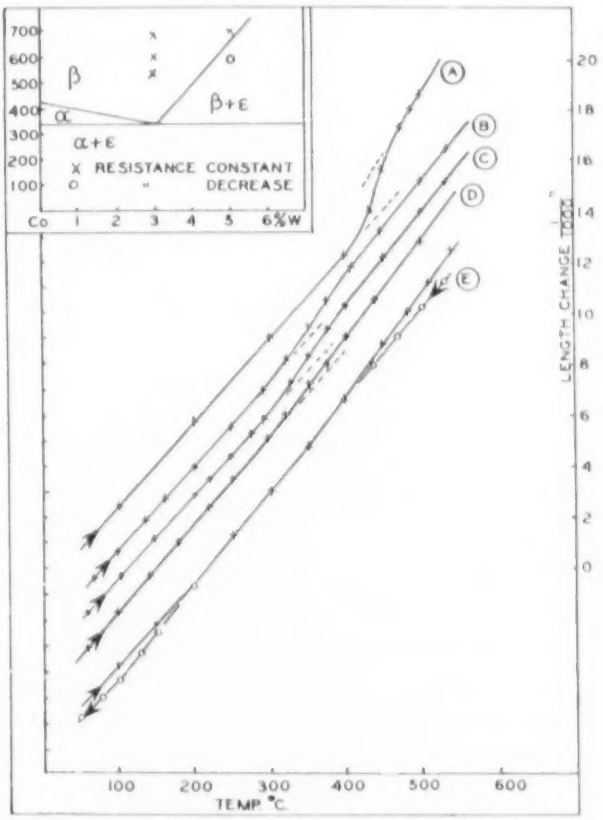


Fig. 4—Expansion Curves of Cobalt and Cobalt-Tungsten Alloys. A—Cobalt; B—Cobalt, 3 Per Cent Tungsten; C—Cobalt, 5 Per Cent Tungsten; D—Cobalt, 10 Per Cent Tungsten. A, B, C and D Previously Cooled from 1000 to 300 Degrees Cent. in 150 Hours. E—Cobalt, 10 Per Cent Tungsten Previously Heated at 1000 Degrees Cent. for 25 Hours and Quenched.

series of alloy wires. These wires were produced from alloys melted in hydrogen and subsequently hot-rolled, swaged, and drawn to a finished diameter which varied among the several lengths between 0.0250 and 0.0251 inch. These alloys harden rapidly with working, and it was found necessary to anneal the 15 and 18 per cent molybdenum wires twice while drawing from 0.060 to 0.025 inch in diameter. Attempts to finish the 20 per cent molybdenum alloy by drawing were unsuccessful.

To insure the formation of the single phase solid solution the wires in six inch lengths were heated for 5 hours in hydrogen at 1300 degrees Cent. (2370 degrees Fahr.) and cooled in hydrogen to room temperature. (From 1300 to about 500 degrees Cent. (2370-930 degrees Fahr.) in 30 seconds). Three specimens of each composition were so heated, each wire being inserted in a small silica tube. The identity of each specimen was preserved by suitable marking so that its resistance might be followed throughout subsequent treatments. The apparatus and procedure involved in the measurements have been previously described (4).

Table I

Specific Electrical Resistivity at 25 ± 0.5 Degrees Cent. of Cobalt-Molybdenum Alloys

Per Cent Molybdenum		Resistivity
By Weight	By Atom	Ohms x 10^{-6}
0	0.0 (Cobalt)	10.0
2	1.2	23.3
5	3.1	39.3
10	6.3	54.0
15	9.8	63.4
18	13.5	64.7

These data from wires cooled rapidly in hydrogen after heating at 1300 degrees Cent. (2370 degrees Fahr.) for 5 hours in hydrogen.
Diameter of wire—0.02505 ± 0.00005 inch
Measured length—3.990 inch

In Table I are listed the values for specific resisitivity obtained from this series. The relation between resistivity and molybdenum concentration is represented by the curve in Fig. 5.

A group of wires as cooled rapidly from 1300 degrees Cent. (2370 degrees Fahr.) were subsequently heated in hydrogen for 25 hours at each of a series of temperatures between 1050 and 700 degrees Cent. (1920-1290 degrees Fahr.) to determine the limit of the solid solution field in this temperature range. The wires were cooled rapidly to room temperature as described above and the resistance measurements made at 25 ± 0.5 degrees Cent. In Fig. 6 are shown the results of these measurements. In the compositions between 5 and 18 per cent molybdenum an unexpected increase in resistance was observed after the first 25-hour heating period at the temperatures indicated in the figure. Subsequent heating, however, at these temperatures or lower temperatures resulted in a marked decrease in resistance. The line A-A′ representing the limit of solid solubility is drawn on the assumption that the initial increase in resistance is a phenomenon accompanying the early stages of precipitation.

It was observed that the resistance increased noticeably following each one hour heating period at 1300 degrees Cent. (2370 degrees Fahr.) in the cases of the 5, 10 and 15 per cent molybdenum

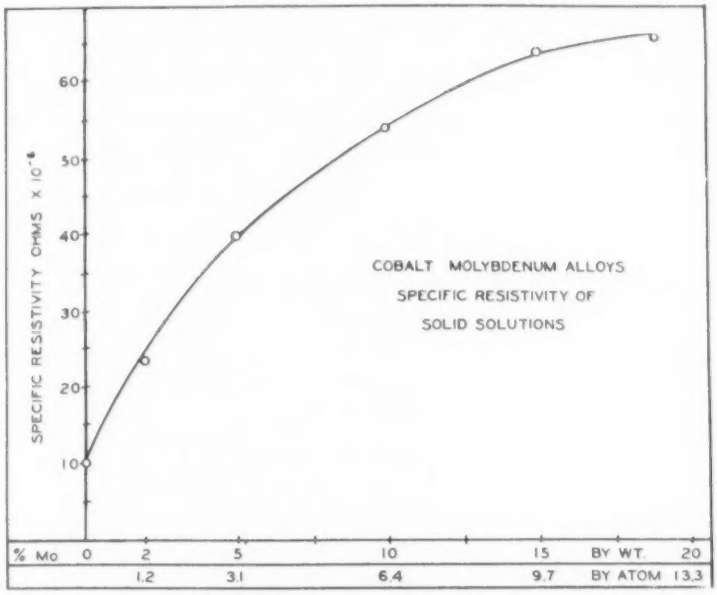


Fig. 5—Specific Resistance of Cobalt-Molybdenum Alloys at 25 ± 0.5 Degrees Cent.

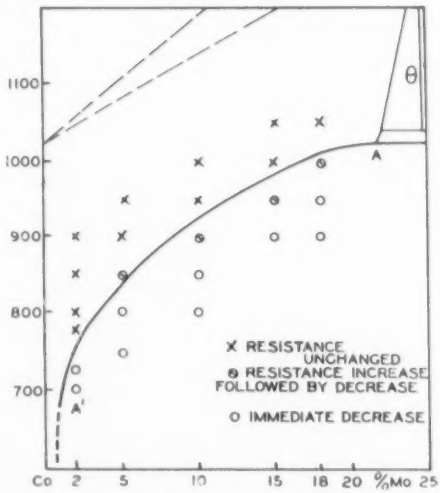


Fig. 6—Solid Solubility as Indicated by Measurements of Electric Resistance.

alloys. This increase persisted throughout further heating at temperatures as low as 1050 degrees Cent. These increases amounted to as much as 1 per cent for each 25-hour heating period. No such increase was observed in the case of the 18 per cent molybdenum

alloy above 1000 degrees Cent. (1830 degrees Fahr.) and was very slight in the 2 per cent molybdenum alloy. The cobalt wire showed no variations in excess of that attributable to experimental errors.

It appeared possible at first that the above mentioned increase might be due to some sort of contamination during the high temperature treatment. Upon reheating the wires to 1300 degrees Cent. (2370 degrees Fahr.), however, the resistance decreased again to a value very closely approaching that obtained after the previous treatment at 1300 degrees Cent. (2370 degrees Fahr.). Time was not available to further study this problem but the suggestion is offered

Table II

Cobalt Treatments (consecutive)	Cobalt Resistance	Cobalt Res. Change	Cobalt 2% Mo Resistance	Cobalt 2% Mo Res. Change
Heated 900 deg. Cent.—1 hr.	0.0320	.....	0.0745	.....
	0.0317	.....	0.0750	.....
Heated 900 deg. Cent.—1 hr.	0.0319	−0.0001	0.0740	−0.0005
	0.0319	+0.0002	0.0744	−0.0006
Heated 900 deg. Cent.—1 hr.	0.0320	+0.0001	0.0745	+0.0005
	0.0320	+0.0001	0.0748	+0.0004
Heated 700 deg. Cent.—15 hrs.	0.0321	+0.0001	0.0624	−0.0121
	0.0320	0.0000	0.0623	−0.0125
Heated 700 deg. Cent.— 5 hrs.	0.0322	+0.0001	0.0583	−0.0041
	0.0322	+0.0002	0.0584	−0.0039
Heated 800 deg. Cent.—25 hrs.	0.0321	−0.0001	0.0628	+0.0045
	0.0322	0.0000	0.0621	+0.0037
Heated 990 deg. Cent.— 1 hr.	0.0321	0.0000	0.0748	+0.0120
	0.0321	−0.0001	0.0752	+0.0131
Heated 1080 deg. Cent.— 1 hr.	0.0322	+0.0001	0.0731	−0.0017
	0.0323	+0.0002	0.0744	−0.0008
Heated 1200 deg. Cent.— 1 hr.	0.0323	+0.0001	0.0743	+0.0012
	0.0322	−0.0001	0.0745	+0.0001

Each value is average of three measurements on single wire.
Wires previously annealed at 1100 to 1150 degrees Cent. (2010-2100 degrees Fahr.) for 5 hours after last drawing operation.

here that such changes in electrical resistance may be the result of a structural disturbance incident to cooling through the γ-β field.

Table II is included to show the changes in resistance observed during a series of treatments in the cases of pure cobalt and the 2 per cent molybdenum alloy. It will be observed that after 3 hours at 900 degrees Cent. (1650 degrees Fahr.) the resistance of the alloy wires has approached a constant value. This decreases markedly after the treatments at 700 degrees Cent. (1290 degrees Fahr.). After reheating at 800 and 990 degrees Cent. (1470-1815 degrees Fahr.) the initial resistance is regained. Note, however, that after heating for 1 hour at 1080 degrees Cent. (1975 degrees Fahr.) a real decrease is observed which disappears after a subsequent treat-

ment at 1200 degrees Cent. (2190 degrees Fahr.) for 1 hour. Note also that the resistance of the cobalt has remained substantially unchanged.

The decrease in resistance of the alloy wire which occurs between heatings at 990 and 1080 degrees Cent. (1815-1975 degrees Fahr.) suggests a possible rearrangement in structure required by the lower end of the two solid solution field as drawn in the diagram (Fig. 7). Corresponding data for the other alloys is not at present sufficiently comprehensive for presentation.

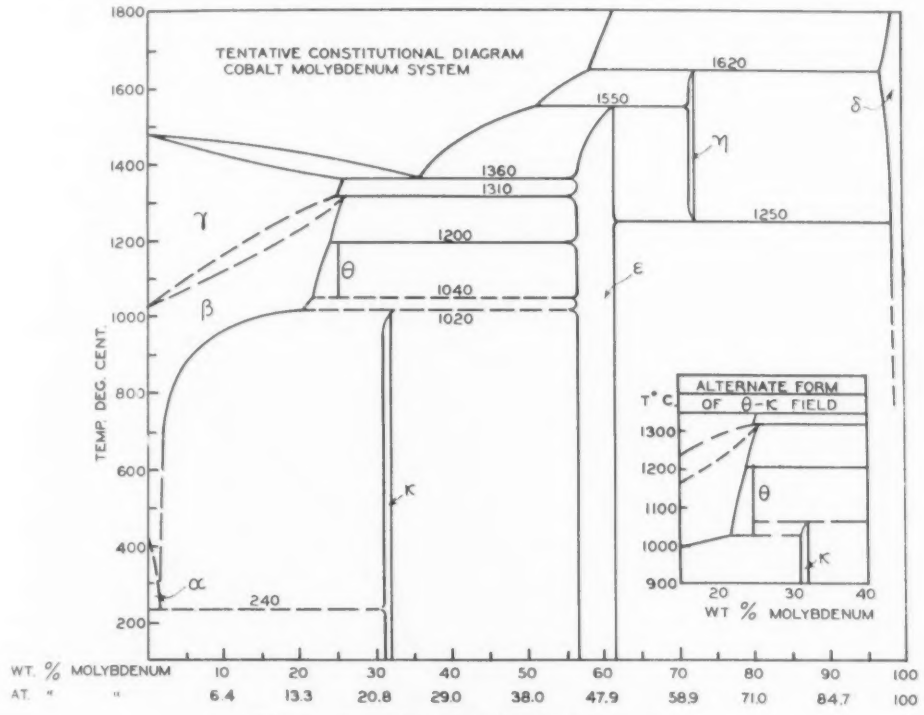


Fig. 7—Tentative Constitutional Diagram.

Constitutional Diagram

A tentative constitutional diagram of the cobalt-molybdenum system is offered in Fig. 7. This is based upon observations of (1) microstructures, (2) diffraction patterns, (3) liquidus and solidus temperatures, (4) electrical resistance and (5) dilatometric data and (6) cooling curves.

The liquidus and solidus temperatures in the cobalt-rich end of the system were first approximated by the conventional freezing curve method. Due to frequent supercooling the resulting data were not entirely satisfactory. The eutectic temperature was how-

ever quite definitely fixed by this method at 1360 ± 5 degrees Cent. (2480 degrees Fahr.). This method of determining the solidus temperature was supplemented by observing the melting points of a series of alloys in wire form when slowly heated in the hydrogen atmosphere as previously described (4). The existence of a peritectic reaction was suggested by the microstructures of homogenized alloys reheated and quenched to determine the solidus. Such a structure is seen in Fig. 8 where the liquid network is bordered by a constituent distinctly different in appearance from the solid phase further removed from the liquid. In contrast to this the 15 per cent molybdenum alloy, Fig. 9, similarly treated shows no such distinct intermediate phase. This evidence is in itself not conclusive for the phenomenon may be merely one of "coring" in which case the difference between the two structures might be attributed to the difference in composition of the alloys. The freezing curves showed no halt corresponding to such a reaction which could be distinguished from the eutectic horizontal and as will be noted later the X-ray evidence indicates the absence of a peritectic reaction. In compositions as low as 23 per cent molybdenum there occurs, even after very slow freezing, a marked segregation of the eutectic-like molybdenum-rich phase which may be completely absorbed by prolonged heating at 1325 to 1350 degrees Cent. (2415-2460 degrees Fahr.) in alloys containing as much as 25 per cent molybdenum.

Such a segregate, bordered by a striated area of solid solution is shown in Fig. 10. As will be mentioned later these etch darkened striations seem to be typical of the cobalt-rich solid solutions supersaturated in molybdenum. The solid solution changes in appearance with increasing molybdenum content as may be observed by comparing Figs. 11 and 12, alloys of 15 and 27 per cent molybdenum respectively which have been quenched after long heating above 1300 degrees Cent. (2370 degrees Fahr.). In the 27 per cent molybdenum alloy the darkly striated phase exists along with a scattering of eutectic (ϵ). By long heating in the range of temperature between 1200 and 1300 degrees Cent. (2190-2370 degrees Fahr.) the cobalt-rich phase undergoes a change as illustrated in Figs. 13 and 14. The darkly striated areas give way to those marked by rectangular bands suggestive of a face-centered cubic form. Note the short needle-like markings in this phase (Fig. 13), suggesting the presence of a precipitate.

The significance of the darkened striations is perhaps better re-

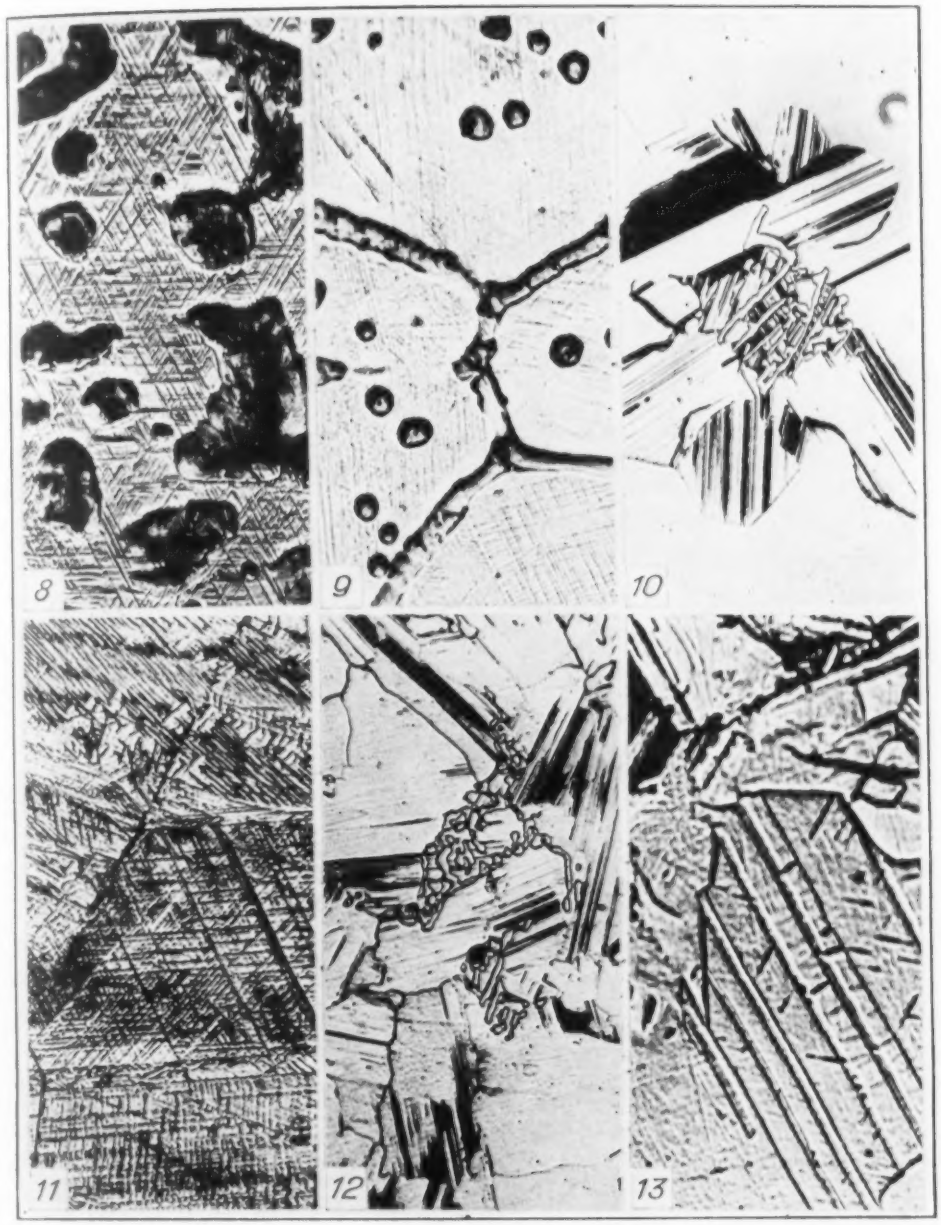


Fig. 8—Cobalt + 20 Per Cent Molybdenum. × 200. Reheated Slowly from 1390 to 1420 Degrees Cent. and Cooled Rapidly. Etched in Aqua Regia.

Fig. 9—Cobalt + 15 Per Cent Molybdenum. × 200. Treated as Specimen Shown in Fig. 8.

Fig. 10—Cobalt + 24 Per Cent Molybdenum. × 200. Alloy After Freezing was Held at 1300 ± 15 Degrees Cent. for 25 Hours and Quenched. Etched in H_2O_2 + H_3PO_4 (4 : 1).

Fig. 11—Cobalt + 15 Per Cent Molybdenum. × 200. Reheated 1320 ± 10 Degrees Cent. 50 Hours After Rolling. Quenched from 1320 Degrees Cent. Etched in Aqua Regia.

Fig. 12—Cobalt + 27 Per Cent Molybdenum. × 200. Quenched from 1330 Degrees Cent. After Heating 50 Hours at this Temperature. Etched in H_2O_2 + H_3PO_4.

Fig. 13—Cobalt + 27 Per Cent Molybdenum. ×200. Heated for 50 Hours at 1330 then for 125 Hours at 1250 Degrees Cent. and Quenched. Etched in H_2O_2 + H_3PO_4.

vealed by the structural changes occurring within the γ phase of alloys near the eutectic composition. In Fig. 15 is shown such an alloy, frozen slowly then cooled from 1325 degrees Cent. (2415 degrees Fahr.) to room temperature in about 3 minutes. Note the darkened striations in the primary cobalt-rich areas. After reheating this specimen at 1275 degrees Cent. (2325 degrees Fahr.) for 30 minutes and quenching, the cobalt-rich areas undergo the change illustrated by Figs. 15, 16 and 17. The darkened bands are now much less numerous than before and have been replaced by well defined globules of the ϵ phase.

Note in Fig. 17 that the inner portion of the cobalt-rich area is still marked by a few darkened bands which might be described as "spindle shaped." There appears morever to be a well defined boundary separating the central banded portion from the surrounding areas in which have formed globules of ϵ. From these structures it may be assumed at least that the darkening seen in Fig. 15 results from precipitation of ϵ in the solid solution during cooling below 1350 degrees Cent. (2460 degrees Fahr.). The formation of β by the reaction $\gamma + \epsilon \leftrightarrows \beta$ may contribute to the structural changes involved here, in which case the globules of ϵ must result from decreased solubility of molybdenum in β at 1275 degrees Cent. (2325 degrees Fahr.).

Primary crystals of ϵ are shown in Fig. 18 in a matrix of the eutectic. Some of the γ phase here has been darkened by precipitation during cooling. This ϵ phase appears from the microstructure to extend over the composition range between 55 and 62 per cent molybdenum. It corresponds to the formula CoMo, the theoretical composition of which is 61.9 per cent molybdenum and may be formed quite completely from the mixed metal powders by long sintering at temperatures near 1500 degrees Cent. (2730 degrees Fahr.). The structure of this phase so formed is shown in Fig. 19. It is marked by the cracks and voids which are typical of intermetallic phases formed in this manner. In the presence of other constituents the ϵ phase may be identified by etching in a boiling sodium picrate solution whereby it is rapidly attacked and appears as shown in Fig. 20.

When heated above 1550 degrees Cent. (2820 degrees Fahr.) ϵ decomposes into cobalt-rich liquid and the solid η phase. The composition of η appears to lie at about 71 per cent molybdenum which approximates the theoretical Co_2Mo_3 of which the molybdenum con-

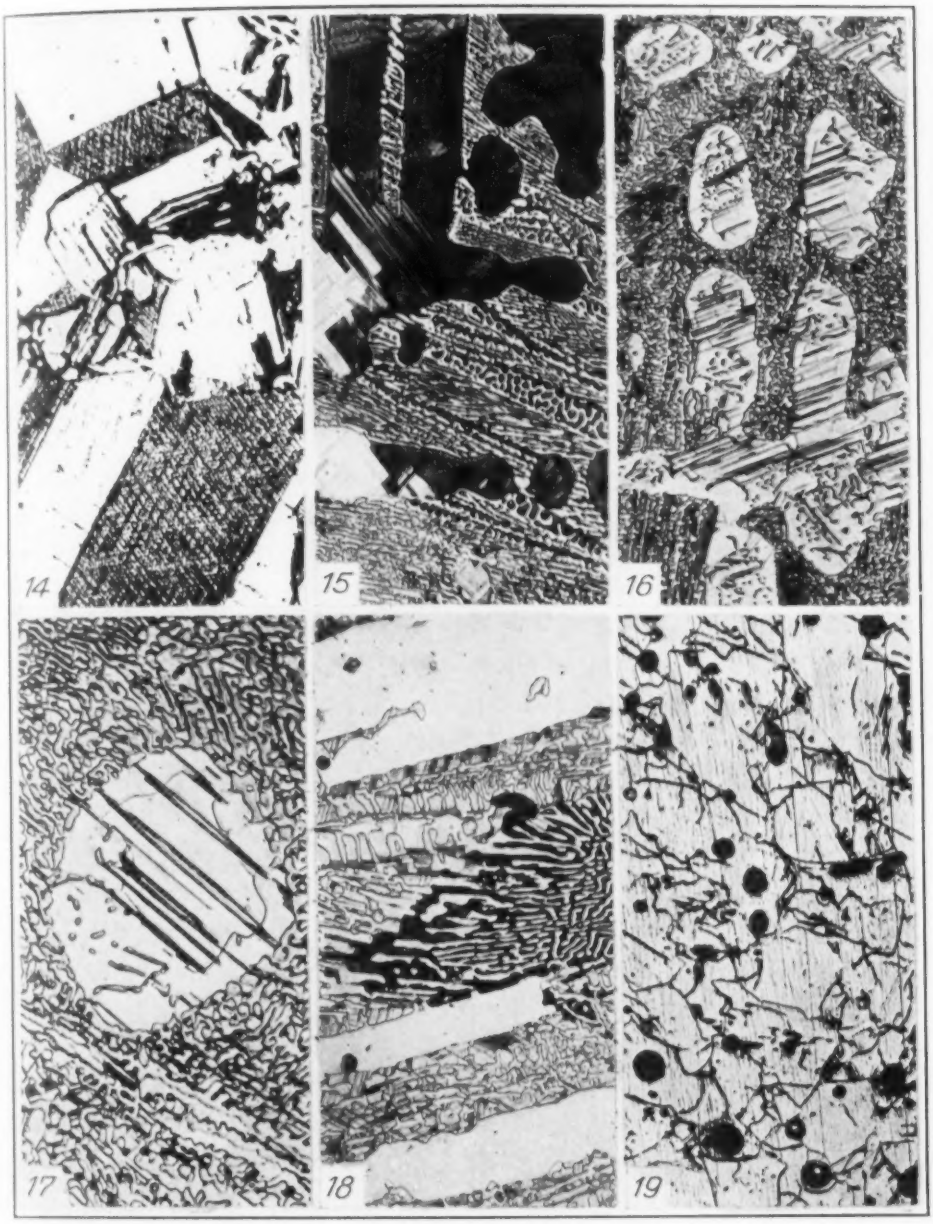


Fig. 14—Same Specimen as Shown in Fig. 13. × 200. Etched in Aqua Regia.

Fig. 15—Cobalt + 36 Per Cent Molybdenum. × 200. Frozen in Furnace and Air Cooled from About 1350 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

Fig. 16—Cobalt + 36 Per Cent Molybdenum. × 200. Treated as Specimen in Fig. 15 then Reheated at 1275 Degrees Cent. and Quenched. Etched in H_2O_2 + H_3PO_4.

Fig. 17—Same Specimen as Shown in Fig. 16. × 500.

Fig. 18—Cobalt + 40 Per Cent Molybdenum. × 200. Cooled in Air After Freezing.

Fig. 19—62 Per Cent Molybdenum, 38 Per Cent Cobalt. (The ε phase). × 200. Sintered 25 Hours at 1325 Degrees Cent. and 25 Hours at 1510 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

tent is 70.9 per cent by weight. This phase appears as a core of primary solid in alloys containing molybdenum slightly in excess of 50 per cent which have been rapidly frozen after complete fusion. Such a structure is seen in Fig. 21 and while no precise limits could be determined from the microstructures this phase appears to extend over a very narrow range of composition. The phase is stable between 1620 ± 10 and 1250 ± 20 degrees Cent. (2950-2280 degrees Fahr.). At the higher temperature it decomposes upon heating into the cobalt-rich liquid and the molybdenum-rich solid δ. When cooled below 1250 degrees Cent. (2280 degrees Fahr.) η decomposes into ϵ and δ. The latter reaction takes place rather slowly and for completion requires several hours heating at 1200 degrees Cent. (2190 degrees Fahr.) The etch-darkened areas resulting from this decomposition are shown in Fig. 22. Note that these darkened rings represent the location of η formed during freezing by the reaction at 1620 degrees Cent. (2950 degrees Fahr.) between the primary δ solid and the surrounding cobalt-rich liquid. The cores of δ within the darkened areas are easily identified, while on the outside the rings are bordered by a cobalt-rich constituent approaching ϵ in composition.

Molybdenum dissolves some 3 per cent of cobalt at 1600 degrees Cent. (2910 degrees Fahr.). Alloys containing 5 per cent cobalt which have been sintered at 1550 to 1600 degrees Cent. (2910 degrees Fahr.) for 100 hours show a slight amount of excess cobalt in the form of η islands. Upon heating such an alloy above 1620 degrees Cent. (2950 degrees Fahr.) and cooling rapidly the liquid network is preserved as seen in Fig. 23. Slow cooling through this peritectic range allows the re-formation of η.

This is shown in Fig. 24 along with globules of η which have precipitated from the δ solid solution during cooling to 1325 degrees Cent. (2415 degrees Fahr.). In such an alloy after further cooling to a temperature below 1250 degrees Cent. (2280 degrees Fahr.) the η areas are seen to have decomposed and darken upon etching as will be noted in Fig. 25.

The Intermediate Phases in the Cobalt-Rich Region

In alloys containing more than 24 per cent molybdenum a marked change occurs in the appearance of the solid solution upon cooling below 1200 degrees Cent. (2190 degrees Fahr.). The cobalt-rich phase β, always heavily marked by twinning bands (Fig. 26) is replaced by a phase which is highly resistant to both the phosphoric

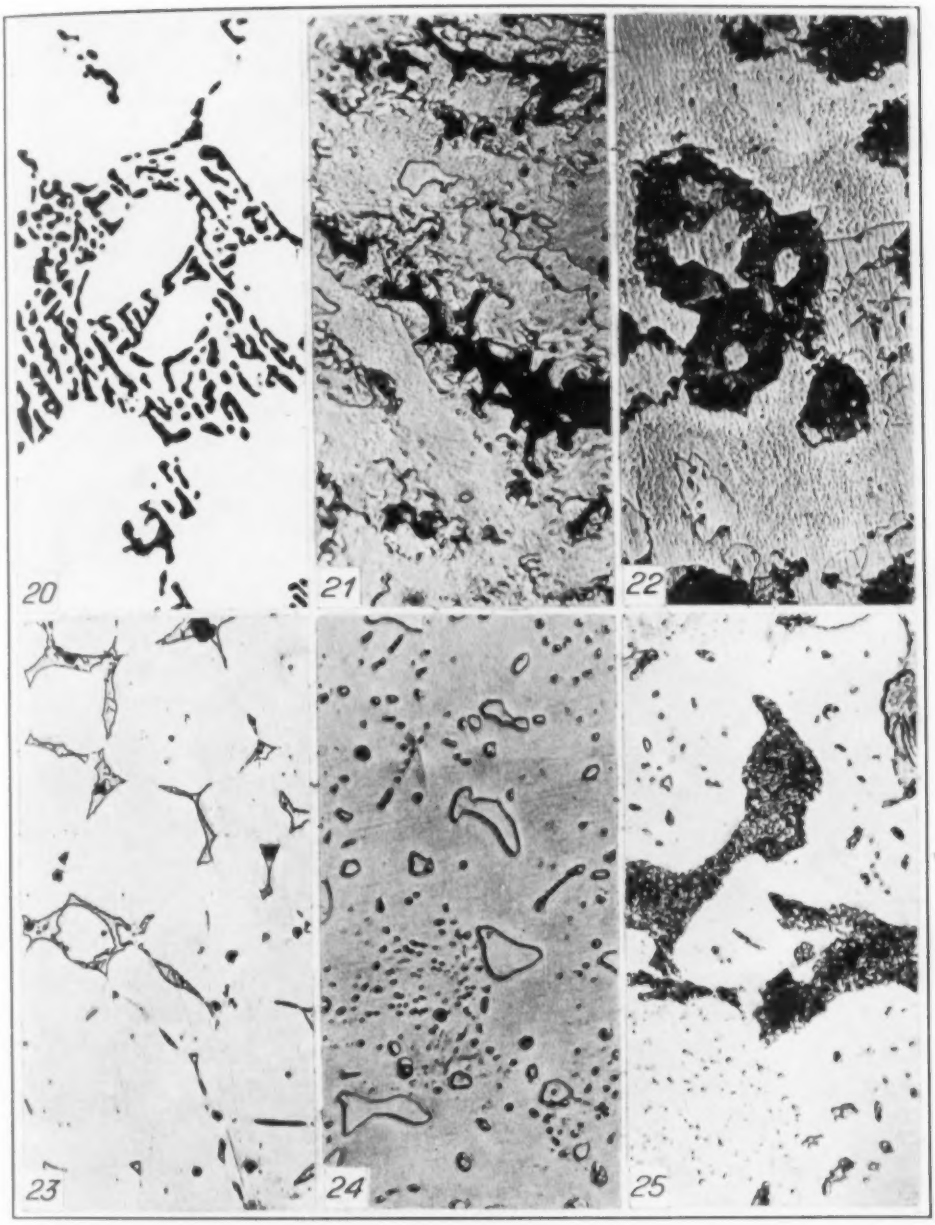


Fig. 20—Cobalt + 30 Per Cent Molybdenum. × 200. Quenched from 1300 Degrees Cent. After Freezing. (ε) in Eutectic Etched Away in Boiling Sodium Picrate.

Fig. 21—Cobalt + 55 Per Cent Molybdenum. × 500. Cooled Rapidly from 1650 Degrees Cent. Etched in H_2SO_4 + HNO_3.

Fig. 22—70 Per Cent Molybdenum, 30 Per Cent Cobalt. × 200. Partial Fusion. Cooled After Freezing from 1450 to 1100 Degrees Cent. in 3 Hours. Quenched from 1100 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

Fig. 23—95 Per Cent Molybdenum, 5 Per Cent Cobalt. × 200. Sintered 50 Hours 1350 to 1500 Degrees Cent. Heated to 1630 Degrees and Cooled Rapidly to Room Temperature. Etched in H_2O_2 + H_3PO_4.

Fig. 24—95 Per Cent Molybdenum, 5 Per Cent Cobalt. × 500. Cooled from 1630 to 1325 Degrees Cent. in 3 Hours and Quenched from Latter Temperature. Etched in Aqua Regia.

Fig. 25—95 Per Cent Molybdenum, 5 Per Cent Cobalt. × 500. Cooled from 1630 to 1325 Degrees Cent. in 3 Hours. From 1325 to 1100 Degrees Cent. in 1 Hour. Quenched from 1100 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

acid and the aqua regia etchant. It is characterized by large grains crossed here and there by cracks of appreciable width as may be seen in Fig. 27. This phase, Θ, appears to have a composition of about 25 per cent molybdenum but precise determination is hampered by apparent difficulty in attaining equilibrium in the solid solution at temperatures between 1200 and 1350 degrees Cent. (2190-2460 degrees Fahr.). This phase first appears in the 23 per cent molybdenum alloy which after long heating above 1300 degrees Cent. (2370 degrees Fahr.) is very slowly cooled to about 1150 degrees Cent. (2100 degrees Fahr.) and held at this temperature for many hours. It is seen as the light areas in Fig. 28 in which the cobalt-rich matrix has been severely attacked by the aqua regia etchant. With increasing molybdenum the cobalt-rich solid solution β is rapidly replaced by Θ in the range of temperature between 1050 and 1200 degrees Cent. (1920-2190 degrees Fahr.). This phase seems to separate from β in the form of plates (Fig. 29). As the molybdenum content nears 25 per cent the remaining β is seen in the narrow banded seams shown in Fig. 30.

When cooled below 1050 $\pm$ 10 degrees Cent. (1920 degrees Fahr.) Θ appears to undergo a decomposition which results in a darkly etched structure shown in Figs. 31 and 32. Excess β is seen in the former and excess ϵ in the latter of these photomicrographs as the lighter constituent. When only a small amount of Θ is present above 1050 degrees Cent. (1920 degrees Fahr.) as in the 23 per cent molybdenum alloy of Fig. 28, the decomposition which attends cooling below 1050 degrees Cent. (1920 degrees Fahr.) results in a structure illustrated in Fig. 33. Here the larger pre-existing plates of Θ have darkened completely while some precipitation has occurred in the β solid solution as evidenced by network of darkened bands. Note that this alloy had been cooled from 1140 to 1000 degrees Cent. (2085-1830 degrees Fahr.) in 10 minutes and then quenched from the latter temperature. This specimen was etched with the relatively mild phosphoric acid reagent while that shown in Fig. 28 was deeply etched with aqua regia which attacks the β phase rapidly.

The true nature of the reaction by which Θ decomposes is obscured by a second reaction which seems to occur at a temperature very slightly below that of the first. It has not been found possible to isolate the two reactions because of the difficulty in maintaining the temperature constant within $\pm$ 15 degrees Cent. throughout heat-

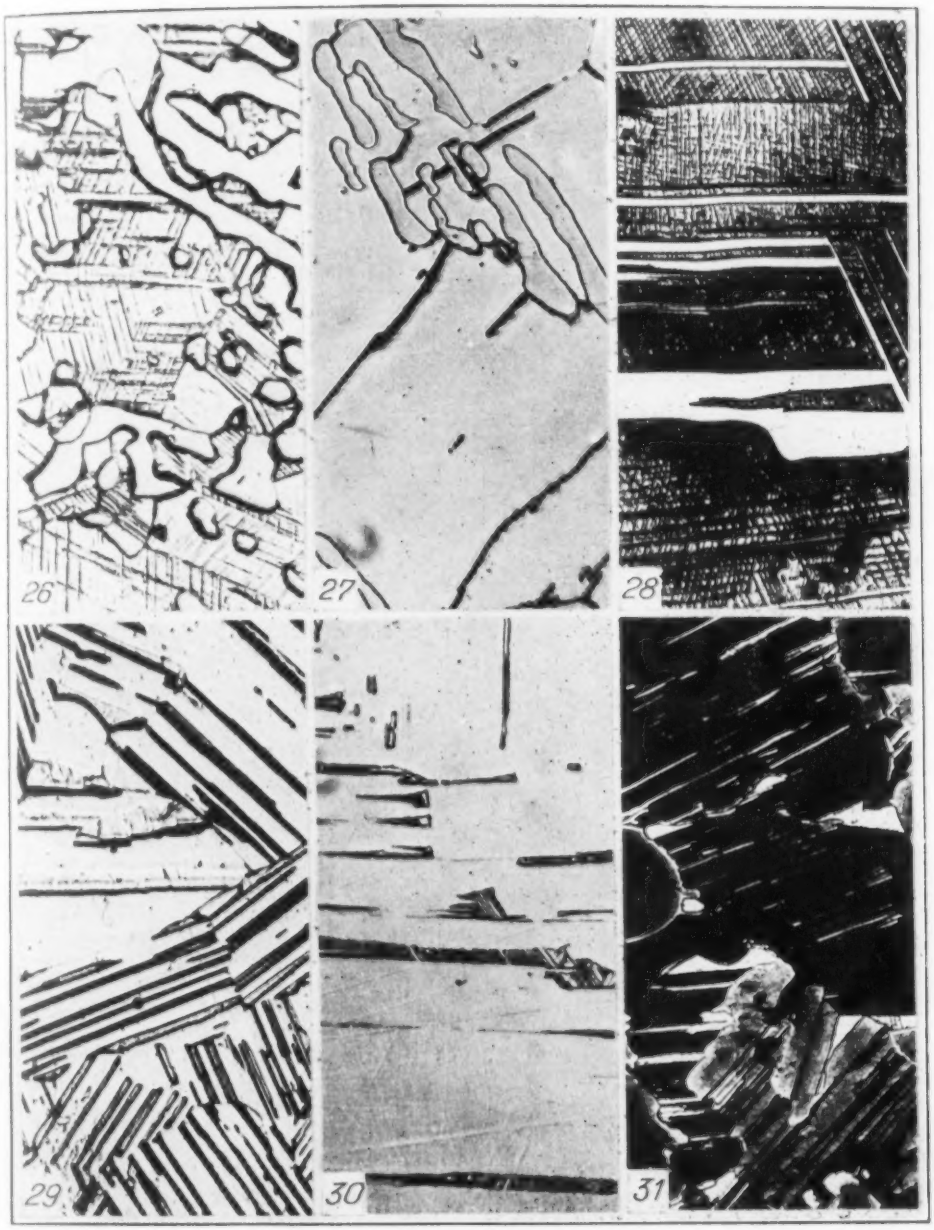


Fig. 26—Cobalt + 32 Per Cent Molybdenum. × 500. Heated 25 Hours at 1325 Degrees Cent. and 25 Hours at 1225 Degrees Cent. and Quenched. Aqua Regia Etch.

Fig. 27—Cobalt + 32 Per Cent Molybdenum. × 500. After Heating at 1325 and 1225 Degrees Cent. as in Fig. 26 this Specimen was Cooled to 1190 ± 10 Degrees Cent., Held at this Temperature for 20 Hours and Quenched. Aqua Regia Etch.

Fig. 28—Cobalt + 23 Per Cent Molybdenum. × 200. Heated for 50 Hours at 1340, 1250 and 1150 Degrees and Quenched from 1150 Degrees Cent. Aqua Regia.

Fig. 29—Cobalt + 24 Per Cent Molybdenum. × 200. Heated for 50 Hours at 1340, 1250, 1225 and 1125 Degrees Cent. and Quenched from 1125 Degrees Cent. Etched in $H_2O_2 + H_3PO_4$.

Fig. 30—Cobalt + 24.5 Per Cent Molybdenum. × 500. Heated 50 Hours at 1340, 1250, 1125 and 1100 Degrees Cent. Quenched from 1100 Degrees Cent. Etched in $H_2O_2 + H_3PO_4$.

Fig. 31—Cobalt + 24 Per Cent Molybdenum. × 200. Heated for 50 Hours at 1340, 1250, 1225 and 1125 Degrees Cent. Cooled from 1125 Degrees Cent. to 1000 Degrees Cent. in 10 Minutes and Quenched. Etched in $H_2O_2 + H_3PO_4$.

ing periods of 100 or 200 hours. The diagram is drawn to represent Θ decomposing into β and ε though the evidence might equally well support the form inserted in the lower corner of Fig. 7. The granular nature of the structure resulting from the decomposition is shown in Fig. 34. This specimen was cooled from 1100 to 1030 degrees Cent. (2010-1885 degrees Fahr.) in 10 minutes, held at the latter temperature for 30 minutes and quenched. One constituent of this duplex structure appears to be continuous with the residual seams of the cobalt-rich β phase. After prolonged heating at 1000 ± 15 degrees Cent. a new phase (K) is observed which obviously results from a reaction between β and ε and the composition of which is estimated to lie near 32 per cent molybdenum. The progress of this reaction is shown in Figs. 35, 36 and 37 which are the structures observed in a eutectic alloy previously heated at 1025 degrees Cent. to decompose Θ. In Fig. 35 the lighter areas represent ε surrounded by the products of the Θ decomposition. After further heating at 1000 degrees Cent. the second reaction has resulted in a localized formation of a second light etching phase surrounding the original eutectic ε (Fig. 36). Further heating for 200 hours at 975 to 1000 degrees Cent. has almost completely eliminated the darkened areas which were originally Θ while the ε phase has noticeably decreased in quantity. The structure now is almost completely composed of ε and K as shown in Fig. 37.

The precipitation hardening which occurs during aging at 700 degrees Cent. results in structures illustrated in Figs. 38, 39 and 40. This alloy of 20 per cent molybdenum had been hot rolled, homogenized at 1300 degrees Cent. for 50 hours and quenched. The Rockwell hardness after this treatment measured C 23. After aging for 5 hours at 700 degrees Cent. (1290 degrees Fahr.) the hardness had increased to C 27 and the structure showed evidence of precipitation (Fig. 38). After 15 hours at 700 degrees Cent. (1290 degrees Fahr.) the hardness measured C 35 while the areas darkened presumably by precipitated K had grown outward from the grain boundaries as shown in Figs. 39 and 40. The darkened lines throughout the solid solution presumably mark the earlier stages of precipitation.

Hardness Characteristics

As shown in Fig. 41 the hardness of the cobalt-rich solid solutions increases with the concentration of molybdenum up to about

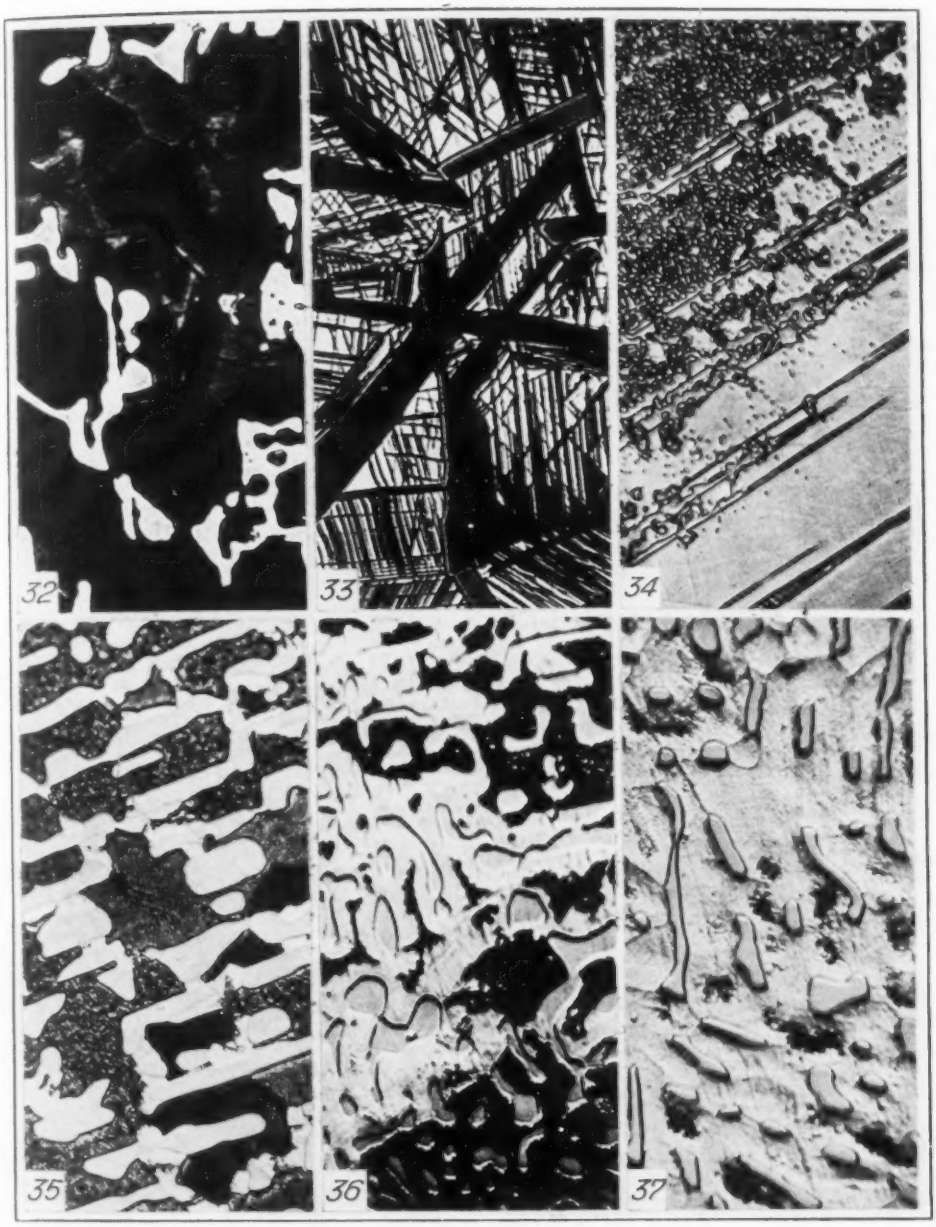


Fig. 32—Cobalt + 29 Per Cent Molybdenum. × 200. Heated for 50 Hours at 1325 and 1150 Degrees Cent. Cooled from 1150 to 1000 Degrees Cent. in 10 Minutes. Quenched from 1000 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

Fig. 33—Cobalt + 23 Per Cent Molybdenum. × 200. After Rolling Heated 50 Hours at 1325, 1225 and 1150 Degrees Cent. and Cooled from 1150 to 1000 Degrees Cent. in 10 Minutes. Quenched from 1000 Degrees Cent. Etched in H_2O_2 + H_3PO_4.

Fig. 34—Cobalt + 24.5 Per Cent Molybdenum. × 500. Heated 50 Hours at 1340, 1250 and 1100 Degrees Cent. Cooled from 1100 to 1025 Degrees Cent. Held at this Temperature for 30 Minutes and Quenched. Etched in H_2O_2 + H_3PO_4.

Fig. 35—Cobalt + 36.5 Per Cent Molybdenum. × 1000. Heated for 25 Hours at 1100 Degrees Cent. and Cooled to 1025 Degrees Cent. in 3 Hours. Quenched from 1025 Degrees Cent. Etched in Aqua Regia.

Fig. 36—Cobalt + 36.5 Per Cent Molybdenum. × 1000. Heated for 50 Hours at 1100 Degrees Cent. Cooled from 1100 to 1000 Degrees Cent. in 3 Hours, Held at 1000 Degrees Cent. for 2 Hours and Quenched. Etched in Aqua Regia.

Fig. 37—Cobalt + 36.5 Per Cent Molybdenum. × 1000. In Addition to Treatment Described Under Fig. 36, this Specimen was Heated at 975 Degrees Cent. for 200 Hours and Quenched. Etched in Aqua Regia.

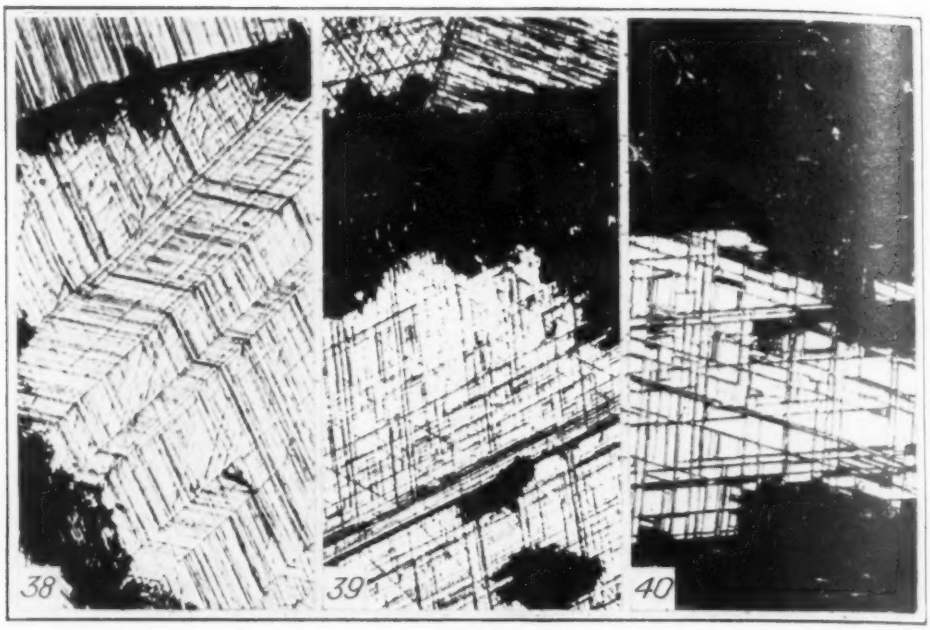


Fig. 38—Cobalt + 20 Per Cent Molybdenum. × 200. After Rolling Heated at 1325 Degrees Cent. for 50 Hours, Quenched and Aged 5 Hours at 700 Degrees Cent. Hardness Increased from C 23 to C 27 During Aging. Etched in H_2O_2 + H_3PO_4.
Fig. 39—Cobalt + 20 Per Cent Molybdenum. × 200. Aged 15 Hours at 700 Degrees Cent. Hardness After 15 Hours Aging, C 35.
Fig. 40—Same as Fig. 39. × 500.

20 per cent of the latter component. These data were obtained from alloys formed from the mixed powders sintered for several hours at 1300 to 1325 degrees Cent. (2370-2415 degrees Fahr.) and quenched.

The hardness increase might be expected to continue up to some 25 per cent molybdenum, the limit of solid solubility at 1350 degrees Cent. (2460 degrees Fahr.). Other factors are here involved, however, which tend to lower the apparent hardness in this range of composition. It appears impossible to obtain an alloy free from undue porosity and segregation even after prolonged sintering in the range between 20 and 40 per cent molybdenum. This difficulty has been encountered in attempting to alloy other metal powders by the sintering process.

Cast alloys of 25 to 30 per cent molybdenum content tend to freeze with segregation of the eutectic constituent, and even after a long homogenizing treatment the hardness of such a composition is nonuniform.

As the molybdenum content approaches 40 per cent the Rockwell hardness of the sintered alloy attains a maximum of C 59 or 60.

falling again at 55 per cent molybdenum to about C 15 as the amount of the intermetallic phase ϵ increases rapidly. Sintered compositions in the range 55 to 75 per cent molybdenum are capable of scratching glass, though unsuited, because of brittleness, to indentation methods of hardness measurement.

In the field of the molybdenum-rich solid solution the hardness increases enormously with the first additions of cobalt, attaining a

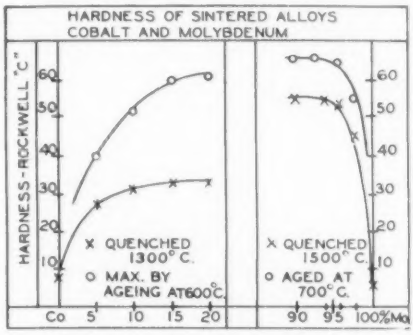


Fig. 41—Hardness of Sintered Alloys.

maximum C 63 in the 6 per cent cobalt composition. As the constitutional diagram indicates, this composition lies considerably beyond the field of the molybdenum-rich solid solution and contains an appreciable quantity of the intermetallic phase η.

For the purpose of hardness determinations and the observation of working characteristics, alloys in the cobalt-rich solid solution range were melted and allowed to solidify slowly in the furnace. In most cases it was found necessary to remelt in order to eliminate nonmetallics and gas pockets, this being followed by an homogenizing treatment of 25 to 50 hours at 1300 to 1325 degrees Cent. (2370-2415 degrees Fahr.).

After such treatment the hardness of the alloys as quenched from 1300 degrees Cent. was found to be lower by several points than that of the sintered alloys of like composition. This difference is probably due to the much smaller grain size of the sintered alloys. The presence of the eutectic with its accompanying ϵ phase results in a marked increase in the hardness of the cast alloys and the complete eutectic composition (36.5 per cent molybdenum) has a hardness of C 55 as cast.

Age Hardening

The cobalt-rich alloys as quenched from above 1200 degrees Cent. (2190 degrees Fahr.) begin to harden slowly when aged at

500 degrees Cent. (930 degrees Fahr.) but attain their maximum hardness only after some 500 hours at this temperature. At 550 degrees Cent. (1020 degrees Fahr.) the increase is more rapid as shown in Fig. 42 and at 700 degrees Cent. (1290 degrees Fahr.)

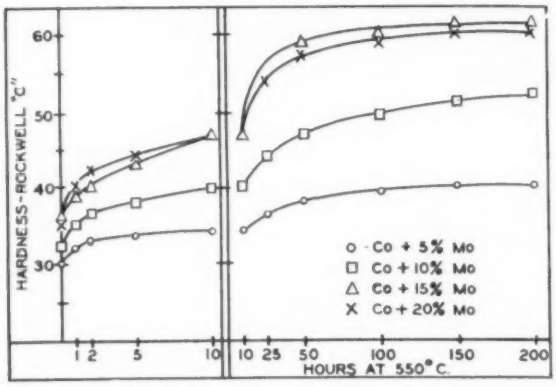


Fig. 42—Age Hardening at 550 Degrees Cent.

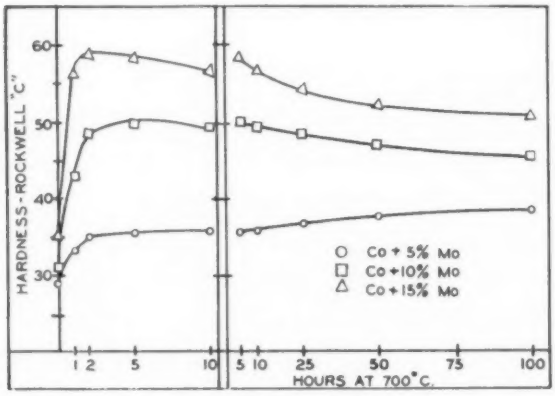


Fig. 43—Age Hardening at 700 Degrees Cent.

the maximum hardness has been passed at the end of 5 hours in the alloys of 10 and 15 per cent molybdenum. (Fig. 43).

The relation between hardness, aging time and temperature of aging is shown for the sintered alloy of 15 per cent molybdenum in Fig. 44. An optimum aging temperature of 600 degrees Cent. (1110 degrees Fahr.) is indicated from these curves since after 25 hours at this temperature the hardness is nearly equal to the maximum developed by aging at 550 degrees Cent. (1020 degrees Fahr.) for 100 hours.

The molybdenum-rich alloys containing up to 10 per cent cobalt attain their highest hardness after aging 25 hours at 700 degrees Cent. (1290 degrees Fahr.).

Cast alloys containing up to 23 per cent molybdenum may be rolled and swaged at 1100 to 1200 degrees Cent. (2010-2190 de-

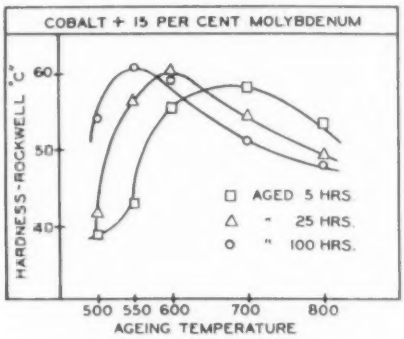


Fig. 44—Hardness Versus Time and Temperature of Aging.

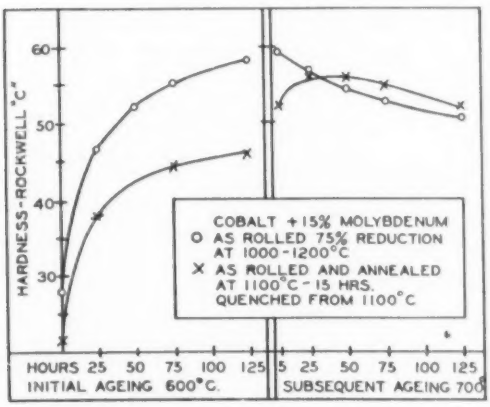

HARDNESS - ROCKWELL "C"
60
50
40
30
COBALT + 15% MOLYBDENUM
○ AS ROLLED 75% REDUCTION AT 1000 - 1200°C
× AS ROLLED AND ANNEALED AT 1100°C - 15 HRS. QUENCHED FROM 1100°C
HOURS 25 50 75 100 125 5 25 50 75 100 125
INITIAL AGEING 600°C.
SUBSEQUENT AGEING 700

Fig. 45—Age Hardening in Alloys as Annealed and as Hot-worked.

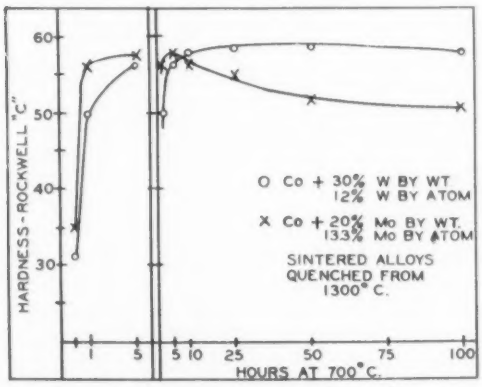

HARDNESS - ROCKWELL "C"
60
50
40
30
○ Co + 30% W BY WT. 12% W BY ATOM
× Co + 20% Mo BY WT. 13.3% Mo BY ATOM
SINTERED ALLOYS QUENCHED FROM 1300° C.
1 5 5 10 25 50 75 100
HOURS AT 700° C.

Fig. 46—Comparison of Cobalt-Tungsten and Cobalt-Molybdenum Alloys Age Hardened at 700 Degrees Cent.

grees Fahr.). Considerable hardening results from this operation and as shown in Fig. 45 the alloy as-worked hardens more rapidly

by aging at 600 degrees Cent. (1110 degrees Fahr.) than one which has received an annealing or solution treatment following the working.

The 15 per cent molybdenum alloys represented in Fig. 45 were first aged to near maximum hardness at 600 degrees Cent. (1110 degrees Fahr.), one as hot-rolled and the other as-rolled and annealed at 1100 degrees Cent. (2010 degrees Fahr.). They were subsequently aged at 700 degrees Cent. (1290 degrees Fahr.). It is of interest to note that the hardness of the alloy as rolled begins to decrease after 5 hours at 700 degrees Cent. (1290 degrees Fahr.) while that of the annealed alloy is still increasing, though after 125 hours they are of very nearly the same hardness.

A comparison of the cobalt-molybdenum alloys with those of the cobalt-tungsten system indicates that the hardening developed by aging in the latter is the more permanent at elevated temperatures. In Fig. 46 are shown the hardening curves of two such alloys aged at 700 degrees Cent. (1290 degrees Fahr.). It will be noted that these alloys of nearly identical atomic concentrations, develop about the same maximum hardness. The molybdenum alloy, however, hardens more rapidly and has begun to soften long before the tungsten alloy has attained its full hardness.

X-Ray Data

The diffraction patterns derived from cobalt metal have been previously described (4), but a brief review of the factors involved may be included profitably at this point. Cobalt metal reduced from the oxide at temperatures between about 450 and 1050 degrees Cent. (890-1920 degrees Fahr.) shows the pattern of the face-centered lattice only. Reduction at temperatures below 450 degrees Cent. results in the close packed hexagonal form. There is no evidence to indicate that cobalt so produced can be completely converted into the face-centered cubic form by subsequent heating for a reasonable period of time in the range from 450 to 1050 degrees Cent. (840-1920 degrees Fahr.). The face-centered cubic form however when subsequently heated above 1050 degrees Cent. (1920 degrees Fahr.) and rapidly cooled shows the combined hexagonal and face-centered cubic patterns. Moreover, the face-centered cubic may be readily converted to the hexagonal form by deformation at room temperature. This evidence suggests that above 1050 degrees Cent. cobalt reverts to the hexagonal form. It is possible, however, that the slight deformation involved in the preparation of the specimen for exposure after the high temperature treatment might account for the appearance of the hexagonal lines in the metal so treated. The question, it appears, can be decided only by a diffraction pattern obtained from the metal while at temperature. The foregoing remarks are meant to serve as a background for subsequent description of the diffraction patterns obtained from alloys consisting wholly or in part of the cobalt-rich solid soluton, designated as β in the constitutional diagram.

It has been observed that the briquetting operation itself involves sufficient deformation to convert the face-centered cubic into the hexagonal form. This fact introduces a disturbing factor when an alloy is to be prepared by the

sintering method for subsequent X-ray analysis. A solid solution which when produced by freezing from the melt might be found to exist at 1325 degrees Cent. in the face-centered cubic form. On the other hand an alloy of the same composition produced by sintering briquetted powders might conceivably be converted to the face-centered cubic form with much difficulty owing to the persistence of the hexagonal lattice of cobalt and the slow attainment of structural equilibrium even at a temperature just under the solidus. Such a condition was encountered in the cobalt-tungsten alloys, although by prolonged sintering saturated solid solutions of tungsten in cobalt were obtained which showed only the face-centered cubic pattern.

In the formation of any binary alloy by the sintering process the attainment of the final state of equilibrium may be considered to result from a progressive change in the composition of each of the two original components. For example, consider a powder mixture of 80 per cent cobalt and 20 per cent molybdenum heated at 1300 degrees Cent. (2370 degrees Fahr.). Complete solution of the molybdenum by diffusion into the solid cobalt will assuredly require considerable time. The concentration of molybdenum in cobalt must increase gradually so that at any moment before equilibrium is established there will exist in the mixture at least two constituents, i.e., (1) cobalt containing less than 20 per cent molybdenum, and (2) a molybdenum-rich constituent. If cobalt exists in the hexagonal form at 1300 degrees Cent. and in this form is capable of dissolving several per cent of molybdenum is it not thinkable that it might become supersaturated in molybdenum in the sense that the hexagonal lattice would persist in the field of composition normally occupied by the face-centered cubic arrangement? This suggestion is made in view of the behavior of pure cobalt previously described. The normal form of such concentrated solutions should in this case be determined from alloys formed by melting and quenched after a long homogenizing treatment at a temperature just below the solidus.

The following description of photograms prepared for precision measurements was contributed by Dr. Kent R. Van Horn who kindly consented to lend his aid in this part of the investigation.

"Diffraction patterns were prepared by the Wedge reflection method of small blocks which had been pressed and sintered at the desired temperatures and subsequently received extended heat treatments at various temperatures. A few photograms were also obtained by this method of melts but this practice could not be generally employed because of the large grain size of the solidified metal. The inaccuracies due to specimen size and variation in penetration are avoided by the Wedge reflection procedure which also permits the further advantage of examining block samples.

"The reflection photograms were produced on a General Electric X-ray apparatus equipped with a molybdenum target tube operating at 30,000 volts and 20 milliamperes. The exposure periods with Eastman diaphax films were from 48 to 72 hours. In measuring the position of the reflections, corrections were made for any dimensional changes in the film by reference to a sodium chloride pattern which was recorded on each photogram. The various lines were rated as to intensity, five degrees of intensity being recognized. The X-ray

Table III
Interplanar Spacings and Line Intensities from Typical Photograms Obtained by Wedge Method

Specimen No. 1 Phase γ (formed by sintering)		Specimen No. 2 γ (formed by melting)		Specimen No. 3 θ		Specimen No. 4 ϵ	
A°	Int.	A°	Int.	A°	Int.	A°	Int.
2.99	V.W.	2.95	V.W.	.....	...	2.342	S
2.85	V.W.	2.84	V.W.	.....	...	2.26	V.W.
2.195	M	2.190	S	2.205	M	2.20	W
2.040	S	2.042	S	2.05	M	2.143	M
1.935	V.S.	1.935	V.S.	1.941	V.S.	2.105	M
1.505	M	1.502	M	1.501	M	2.06	S
1.434	V.W.	1.426	V.W.	1.278	M	2.007	M
1.277	M	1.276	M	1.162	M	1.934	W
1.166	M	1.165	M	1.084	M	1.892	M
				1.066	M	1.808	W
				1.027	W	1.771	V.W.
						1.369	W
						1.324	W
						1.297	M

HISTORY OF SPECIMENS

No. 1. Cobalt + 27 per cent Molybdenum. Alloy prepared by melting. After freezing held 100 hours at 1330 ± 10 degrees Cent. and quenched.

No. 2. Cobalt + 28 per cent Molybdenum. Alloy prepared by sintering briquetted mixture at 1330 ± 10 degrees Cent. for 75 hours. Quenched.

No. 3. Cobalt + 27 per cent Molybdenum. Alloy prepared by melting. After freezing held 100 hours at 1330 ± 10 degrees Cent.; 70 hours at 1230 ± 10 degrees Cent.; 25 hours at 1100 ± 10 degrees Cent. Quenched from 1100 degrees Cent.

No. 4. Cobalt + 62 per cent Molybdenum. Alloy prepared from briquetted mixture of powdered metals sintered 25 hours at 1350 and 25 hours at 1425 degrees Cent.

analysis of the various cobalt-molybdenum alloys revealed the following phases, the interplanar spacings of which are incorporated in Table III.

"1. Pure cobalt which occurs in three allotropic modifications, the room temperature hexagonal type, the intermediate temperature face-centered cubic form, and the high temperature hexagonal cobalt. The parameter measurements have been reported for the first two modifications by Hull (8) and Neuberger (9).

	Face-centered Cubic Cobalt	*Low Temperature Hexagonal Cobalt*
Hull	$a_o = 3.554$ Å	$c_o = 4.105$ Å, $a_o = 2.514$, $\frac{c_o}{a_o} = 1.633$
Neuberger	$a_o = 3.545$ Å	$c_o = 4.072$ Å, $a_o = 2.507$, $\frac{c_o}{a_o} = 1.624$

"2. The hexagonal cobalt solid solution, γ, occurring at elevated temperatures from 0 to 20 per cent molybdenum gives a pattern very similar to the low temperature hexagonal cobalt. The reflections are proportionately displaced toward the smaller diffraction

Table IV
Interplanar Spacings Computed from Reflections Obtained with Iron and with Copper Radiation

(observed)	Hex. Close Packed (calc) hk.l		Face-Centered Cubic (calc) hkl	
2.190	2.176	(10.0)	.....	.....
2.052	2.051	(00.2)	2.051	(111)
1.938	1.920	(10.1)	.....	.....
1.800	.....	.....	1.777	(200)
1.500	1.493	(10.2)	.....	.....
1.264	1.257	(11.0)	1.257	(220)
1.158	1.158	(10.3)	.....	.....
1.100	1.089	(20.0)	.....	.....
1.080	1.072	(11.2)	1.072	(311)
1.066	1.051	(20.1)	.....	.....
1.028	1.026	(00.4)	1.025	(222)

Specimen No. 5. Cobalt 27 Molybdenum. Alloy prepared by melting. Heated 1250 degrees Cent. 50 hours; 1220 degrees Cent. 25 hours; 1330 degrees Cent. 25 hours. Quenched from 1330 degrees Cent.

angles with an increasing molybednum content, indicating an appreciable lattice expansion. The maximum value of a_o is 2.554 Å or 1.7 per cent expansion and 4.101 Å or .31 per cent extension for c_o.* However, the two lines occurring at about 1.48-1.49 Å and 1.15-1.16 Å have much greater intensities, reflecting very weak in the room temperature hexagonal cobalt films and medium in the photograms of this solid solution.

"3. The face-centered cubic cobalt solid solution extending from intermediate temperatures in cobalt up to 1300 degrees Cent. (2370 degrees Fahr.) at a molybdenum concentration of about 25 per cent. The β phase was observed in 10 to 28 per cent molybdenum alloys and is recognized by the face-centered cubic reflections which register an unusually large expansion of the elementary cell due to the introduction of molybdenum. The greatest observed lattice enlargement was revealed in a 28 per cent molybdenum sample, namely, 3.60 Å for the cube edge or 1.4 per cent expansion. The β phase was found in specimens containing 10, 15 and 20 per cent molybdenum together with the hexagonal solid solution γ, after treatment at 1300 degrees Cent.

"4. The hexagonal phase, Θ, occurring in hypoeutectic alloys containing 20, 27, 28 and 30 per cent molybdenum, and in the eutectic mixture of higher molybdenum concentrations in combination with the compound CoMo, ϵ. The patterns of Θ resemble room temperature hexagonal cobalt and the solid solution γ as the majority of the hexagonal reflections occur with the correct intensities and there is a uniform displacement of the lines toward the small

*The averages of the Hull and Neuberger values were used in computing these expansions.

diffraction angles, i.e. showing lattice expansion. However, the two reflections at 1.48-1.49 Å and 1.15-1.16 Å are much more intense in films of Θ than in photograms of hexagonal cobalt and are similar to the corresponding lines in films γ. In addition, the reflection at about 1.04-1.05 Å is more intense (weak to medium) in films of this constituent than in patterns of the other hexagonal phases. There were a few additional, less distinguishable variations between γ and Θ such as the occurrence or disappearance of very weak lines, but the most striking difference in Θ is found in strong reflections from the basal planes occurring at 2.03 Å, in cobalt. All the hexagonal reflections of alloys from 10 to 30 per cent molybdenum are gradually displaced toward the small angles from 0.15 to 0.03 Å with the exception of this line (2.03 Å) which is not proportionately shifted with the increasing molybdenum (0 to 0.015 Å). It is possible with the unaided eye to distinguish between γ and Θ by the position of this reflection in respect to the adjacent lines.

"5. The intermediate phase, ε, occurring at 62 per cent molybdenum and observed as the primary phase in hypereutectic alloys from 36 to 62 per cent molybdenum. This phase has been found with either Θ or β in samples containing about 28 per cent molybdenum. The most distinguishable lines are 2.34Å strong, 2.14 Å medium, 2.10 Å medium, 2.06 Å strong, 2.007 Å medium, etc., all occurring in extremely favorable positions for good reflection thereby making it possible to easily detect a small quantity of ε when present.

"6. A phase, K, occurring at lower temperatures and with molybdenum content from 2 per cent up to the composition of the intermediate phase ε. The constituent, K, was detected in a 15 per cent molybdenum sample after final treatment of 150 hours between 800 and 700 degrees Cent. (1470-1290 degrees Fahr.) together with the face-centered solution β. In higher molybdenum alloys it occurs with ε and is recognized by reflections at 2.13 Å weak medium, 1.89 Å medium, 1.14 Å weak, etc.

"7. The molybdenum-rich intermediate phase η having a very distinctive pattern and occurring at 71 per cent molybdenum and with δ in alloys containing from 72 to 95 per cent molybdenum, after treating above 1250 degrees Cent. (2280 degrees Fahr.).

"8. The molybdenum-rich solid solution δ. The body-centered molybdenum lattice is contracted about 1 per cent when saturated with about 3 per cent cobalt at 1600 degrees Cent. (2910 degrees Fahr.)."

Additional data were supplied by Dr. C. S. Barrett and Mr. E. L. McCandless from an alloy of cobalt 27 per cent molybdenum described as alloy No. 5 under Table IV.

They report in part as follows: "Two surfaces at 90 were ground on the specimen and a series of Debye photograms taken of this edge, using iron, copper and molybdenum targets in a gas X-ray tube. Reflections obtained with molybdenum radiation were not sufficiently distinct to be usable. Reflections from iron and copper radiations are listed in Table IV.

"The experimental values for interplanar distances are compared in the table with values for cobalt computed by Hull (8). The comparison shows that two cobalt-rich phases are present in about equal amounts with considerably more but smaller grains in the hexagonal phase than in the face-centered cubic. Assuming the correctness of Hull's a_0 values, the lattices of both phases are slightly expanded. In the hexagonal phase the a- and c- expansions are unequal, as shown by the low values for the spacing of planes with high c- indices, notably (00.2), (10.3) and (00.4)."

Discussion

It should be noted that specimen No. 5 in Table IV had been heated for some time between 1200 and 1300 degrees Cent. (2190-2370 degrees Fahr.) (the β field) before the final treatment at 1330 degrees Cent. (2425 degrees Fahr). This fact may well account for the presence of both forms of the cobalt-rich solid solution since the reaction shown at 1310 degrees Cent. (2390 degrees Fahr.) ($\gamma + \epsilon \rightleftarrows \beta$) appears to be a sluggish one.

The occurrence of the hexagonal γ form alone in specimens No. 1 and 2 indicates moreover that in these alloys structural equilibrium may be attained by sintering as well as by freezing from the melt. From this evidence the diagram has been drawn to show β forming by a peritectoid reaction at about 1310 degrees Cent. (2390 degrees Fahr.) rather than by a peritectic reaction at a higher temperature as the microstructures might indicate. The microstructures suggest that the reaction $\beta + \epsilon \leftrightarrows \Theta$ proceeds very rapidly in alloys which are cooled directly from above 1310 degrees Cent. (2390 degrees Fahr.) into the temperature range between 1200 and 1050 degrees Cent. (2190-1920 degrees Fahr.). This observation may have a real significance in view of the X-ray evidence which indicates that the Θ phase and the γ phase are barely distinguishable.

It has been observed that alloys which after heating at about 1100 degrees Cent. (2010 degrees Fahr.) showed only the hexagonal Θ phase, can be converted into the face-centered cubic β by reheating in the range of temperature between 1200 and 1300 degrees Cent. (2190-2370 degrees Fahr.). Furthermore the decomposition of Θ below 1050 degrees Cent. (1920 degrees Fahr.) results in the formation of β as indicated by the X-ray photograms. Protracted heating below 1050 degrees Cent. (1920 degrees Fahr.) is necessary to develop the β pattern, and it is most obvious in alloys containing less than 25 per cent molybdenum. The lattice parameter of β as shown in the 15 per cent molybdenum alloy after long heating at 700 to 800 degrees Cent. (1290-1470 degrees Fahr.), (mentioned above by Van Horn) is distinctly smaller than that observed in the same phase formed at 1250 degrees Cent. (2280 degrees Fahr.). This is in accord with the diagram as drawn to show a marked decrease in the solid solubility of molybdenum in cobalt in the low temperature range.

No evidence was found either in the microstructures or in the X-ray photograms to indicate the formation of the hexagonal cobalt-rich phase α by a reaction at 950 degrees Cent. (1740 degrees Fahr.) as shown by Köster and Tonn. The hexagonal phase mentioned by Takei as being formed at 1050 degrees Cent. (1920 degrees Fahr.) may be either Θ or K but can scarcely be identified as the α phase. Further work is necessary in order to reveal completely the nature of the K phase. This should involve compositions of 20 to 40 per cent molybdenum finally treated for long periods at temperatures below 1000 degrees Cent. (1830 degrees Fahr.).

Acknowlegments

The age hardening characteristics of the cobalt-rich alloys were studied by Arthur E. Schowalter* in 1932 at the Cleveland Wire Works Laboratory under the guidance of the authors. His findings were submitted in a thesis to the Case School of Applied Science as partial fulfillment of requirements for the degree of B.S. in Metallurgical Engineering.

A. B. Gladding of the Cleveland Wire Works staff prepared many X-ray photograms which were indispensable to the comprehensive interpretation of the observed microstructures.

*Arthur E. Schowalter is at present associated with the Rotary Electric Steel Company, Detroit.

The authors are greatly indebted to the Aluminum Company of America for the use of diffraction apparatus and especially to Dr. Kent R. Van Horn and C. M. Tucker for the preparation and measurement of patterns from several alloy specimens.

Dr. C. S. Barrett and E. L. McCandless of the Metals Research Laboratory, Carnegie Institute of Technology, contributed most generously to the X-ray data included in this paper.

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DISCUSSION

Written Discussion: By R. H. Harrington, Research Laboratories, General Electric Co., Schenectady, N. Y.

One cannot refrain from commenting upon the uniform excellence of the equilibrium diagram work emanating from this source. Once again these authors make use of many tools in their research, including thermal analysis, dilatometric data, X-ray evidence, microstructure, age-hardening studies, resistivity measurements, etc. Naturally the results are such as to justify one's complete faith in them.

The writer must comment favorably upon the open minds of these authors when any alternative interpretations present themselves, as so plainly indicated in Fig. 7. Of the two possible forms of the θ field indicated in this diagram, the writer, for the present, favors the "alternate form" involving $\theta + K$ field. Unless the evidence is definitely to the contrary, the existence of a single phase over a temperature range, with origin and end in two different temperature fields of the same two phases (neither of which is that of the single phase field in question) is not in complete agreement with the present general theories of heat energy relations with the atomic lattice. The typically sluggish reactions of most alloys of cobalt render them exceedingly difficult to study, especially within narrow temperature ranges.

Written Discussion: By Bruce A. Rogers, metallurgical engineer, 6712 North Central Ave., Chevy Chase, Maryland.

For a number of years it has been a pleasure to observe the series of papers on the constitutional diagrams and properties of the alloys containing tungsten or molybdenum and a metal from the iron group, which has been presented by Mr. Sykes and those who co-operate with him. The present article bears evidence of the same accurate and thorough work which has characterized previous publications. The authors are to be congratulated upon a successful attack upon a surprisingly complex binary system.

One of the most interesting features of this paper is the manner in which X-ray data have been used to substantiate and supplement results obtained by microscopic and other methods. The X-ray spectograph appears peculiarly adapted to investigating alloy systems of this type.

The unexpected increase in resistance which occurs in the cobalt-rich alloys is interesting. Some years ago, while working on some cobalt-tungsten alloys, containing also about 2.5 per cent of iron, the writer noticed a somewhat similar phenomenon for certain temperatures of heat treatment. In the case presented by the cobalt-molybdenum alloys, there is the added peculiarity that the annealing treatments which begin at temperatures along the solubility line appear to be the only ones which produce this effect. The theoretical discussion given by Dr. Merica[1] to explain an increased resistance in certain aged aluminum alloys does not appear to fit this case. If Mr. Sykes has an explanation to offer, I should be interested to hear it.

There is another question which I should like to ask Mr. Sykes and that is to inquire why the alloy shown in Figs 15, 16 and 17, which has the eutectic composition should so slightly resemble an eutectic alloy and whether any heat treatment will produce a more customary appearance?

Author's Reply

It is possible that the true nature of the $\Theta + K$ field in this system may never be determined directly from experimental data, and the authors welcome Dr. Harrington's application of theory to the problem of selecting the more probable form.

Dr. Rogers' request for an explanation of the initial increase in resistance observed in the alloys upon cooling below the line A-A′ (in Fig. 6) is entirely pertinent. The authors have no satisfactory explanation. It appears possible that this phenomenon may, however, be akin to the increase observed during the initial stages of aging at lower temperatures as reported by one of the authors in discussing Dr. Harrington's paper.[2] At first glance it seems hardly possible that the noted increase should be observed at such relatively high temperatures. On the other hand, the effect in both cases may presumably result from the segregation of a new phase. The mechanism of formation of such segregates may be subject to variation depending upon the elements and

[1]P. D. Merica, "The Age-Hardening of Metals," *Transactions*, American Institute Mining and Metallurgical Engineers, Institute of Metals Division, Vol. 99, 1932, p. 13-54.

[2]R. H. Harrington, "The Present Status of Age Hardening," TRANSACTIONS, American Society for Metals, Vol. XXII, June 1934, p. 505.

structural forms involved. The need for further investigation in these ranges of temperature and composition is obviously indicated.

The structures mentioned by Dr. Rogers (Figs. 15, 16 and 17) are those of an alloy of slightly hypoeutectic composition. These fields were selected especially to show areas of excess gamma and for that reason may not appear to be truly representative of a 36 per cent molybdenum composition.

Discussion—The Metastability of Cementite

(Continued from page 156)

The experience reported by Dr. Ziegler is of extreme interest to the writer for it is perhaps the most conclusive case which has ever come into the literature of the graphitization of cementite at ordinary temperatures.

There seems to be no difference of opinion between Dr. Austin and the writer as to the infallibility of thermodynamics when properly applied and when applied to data which are sufficiently correct. It would seem that a reading of the next paragraph beyond that quoted by Dr. Austin to the effect that one or more of the data accepted by Yap must be in error should be sufficient to cause the attentive reader to recognize that the criticism is not of the method of approach but Yap's particular conclusion.

Dr. Chipman also seems to have missed the point of the present contribution; that point is that Yap's claim to have shown conclusively on thermodynamic grounds that cementite should be metastable at some elevated temperature contradicts the facts.

The original paper seems to have made sufficiently clear the reasons for the line of approach chosen by the author. That line of approach does not seem to warrant a lengthy review of all the experimental data in the literature but only of that portion which corroborates Yap's viewpoint. Those who are competent to correct Yap's error from the data discussed by Dr. Chipman had remained silent for two years thus permitting the perpetuation of a fairly serious error.

If the author has, by direct and simple means, corrected this error and if the thermodynamists find no reason to doubt the correctness of the conclusions the desired end seems to have been attained.

The writer has the utmost respect for the thermodynamic viewpoint in metallurgy. He has every desire to further it and he believes it a service to that science, not a criticism, to point out an error due not to thermodynamic reasoning but to an improper experimental starting point. It is unfortunate, but not the fault of thermodynamics, that there are many cases where correct conclusions require data so accurate as to impose a serious handicap on those who have reasoned from these grounds.

PROPERTIES OF SOME CAST ALLOY STEELS

By T. N. Armstrong

Abstract

This paper gives a comparison of the mechanical properties of twenty-five alloy steels of low alloying content and one simple carbon steel, and a comparison of properties after nine different heat treatments. The steels studied were limited to those which give combination of strength and high ductility required in ship castings. Quenching in liquids was not included in the heat treatments because of the impracticability of quenching the intricate castings required in ships' construction.

Introduction

FOR a number of years all large hull castings for government-constructed Naval vessels have been manufactured at the Norfolk Navy Yard. Considerable success had been experienced in using a 0.30 per cent carbon, 1.50 per cent nickel, and 0.60 per cent chromium steel for alloy steel castings until several large castings cracked after being shaken out of the molds and before annealing. These cracks were attributed to brittleness in steel as poor molding practice would have been reflected in types of defects not occurring in these particular castings. To prevent recurrence of this trouble a number of low alloy steels were made and tested to determine what class or classes of steel would have the best mechanical properties for the type of castings manufactured. The ultimate purpose of the work was to find a steel which would be fairly ductile in the cast state and which would give an elongation of 25 per cent in two inches and a yield point of 75,000 pounds per square inch after being double annealed, and at the same time would permit the heat-to-heat variation in analysis common to routine production melts. This paper gives the mechanical properties of a number of steels investigated and a comparison of results obtained by different heat treatments.

Melting Practice

The heats were made in a basic-lined Moore "Lectromelt" elec-

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tric furnace of one-half ton rated capacity. The charge for each heat, 1200 pounds, consisted principally of old ship plates and shapes, with some heavy foundry returns. These heats were made under two slags with no ore additions except in several heats in which low carbon was specified. High recovery of chromium, silicon, and manganese shows that there was little oxidation even in the melt down. Alloys, with the exception of titanium, were added in the furnace under the reducing slag. The pouring temperature range was approximately from 2750 degrees Fahr. (1510 degrees Cent.) to 2850 degrees Fahr. (1565 degrees Cent.). The melter estimated the temperature by spoon test before tapping but the actual temperature was measured with a Leeds and Northrup optical pyrometer as the metal poured over the spout of the furnace. Steel from each heat was poured into two test blocks, each block weighing approximately 350 pounds. The main body of the block consisted of a slab 30 by 9 by 2 inches with twelve coupons 9 by 1½ by 2 inches cast on the bottom side. Test blocks were made in dried sand molds and were poured from a bottom-pour ladle. Coupons were removed from the block with an acetylene torch, heat treated, and machined into test specimens.

Method of Heat Treating and Testing

The specimens were heat treated in an automatic temperature control electric furnace. Insofar as possible, bars from all heats were treated at the same time to eliminate variations in heating and variations in cooling in the annealing treatments. Specimens were held at the temperature of treatment for two hours, cooled in the furnace for annealing, and air-cooled after normalizing and after tempering. This procedure was used excepting in treatment K, wherein the bars were tempered at 1300 degrees Fahr. (705 degrees Cent.) for six hours and cooled in the furnace. Tensile tests were made in an Amsler hydraulic testing machine of 50,000 pounds capacity. Impact tests were made in an Amsler impact machine of 240 foot-pounds capacity, equipped with an Izod head and anvil. Impact bars, all of which were machined from the large (⅞ inch) ends of broken tensile bars, were made 0.394 inch (10 millimeters) square and notched on two adjacent sides. V-type notches were rough machined with one cutter and finish machined with a second cutter that was frequently ground and honed with a radius of 0.01 inch on the points. Specimens for microscopic examination were

Table I
Composition of Steels Tested

Heat Number	Per Cent Carbon	Per Cent Manganese	Per Cent Silicon	Per Cent Nickel	Per Cent Vanadium	Per Cent Chromium	Per Cent Molybdenum	Per Cent Copper
1	0.300	0.701	0.276	.....	.....	.....	.....	.....
2	0.164	2.252	0.108	.....	.....	.....	.....	.....
3	0.222	2.009	0.093	.....	.....	.....	.....	.....
4	0.342	1.515	0.286	.....	0.160	0.469	.....	.....
5	0.330	0.869	0.477	0.459	0.181 Ti	0.190	.....	.....
6	0.234	1.306	0.899	.....	.....	.....	.....	.....
7	0.096	1.505	1.188	.....	.....	.....	.....	.....
8	0.278	1.157	0.877	.....	.....	.....	.....	.....
9	0.284	0.754	0.215	.....	.....	.....	.....	0.820
10	0.147	1.434	1.095	.....	.....	.....	.....	0.340
11	0.268	0.993	0.343	1.259	.....	.....	.....	1.174
12	0.239	1.021	0.312	.....	.....	.....	.....	1.260
13	0.252	1.171	0.283	.....	.....	.....	0.319	.....
14	0.376	0.926	0.236	.....	.....	.....	0.363	.....
15	0.222	1.162	0.161	2.319	.....	.....	.....	.....
16	0.356	0.981	0.166	1.925	.....	.....	0.260	.....
17	0.378	1.074	0.189	2.198	.....	.....	.....	.....
18	0.234	1.439	0.189	1.116	.....	.....	.....	.....
19	0.280	1.407	0.206	1.229	.....	.....	.....	.....
20	0.320	1.203	0.378	2.174	.....	.....	.....	.....
21	0.256	1.465	0.171	1.558	0.159	.....	.....	.....
22	0.302	0.941	0.278	1.454	0.167	.....	.....	.....
23	0.382	1.058	0.247	1.694	0.114	.....	.....	.....
24	0.284	0.883	0.201	1.824	0.129	.....	.....	.....
25	0.230	1.086	0.236	2.210	0.129	.....	0.330	.....
26	0.332	1.053	0.251	1.577	0.101	0.252	.....	.....

taken from the large ends of broken tensile bars opposite the ends used for impact specimens. The results listed in the tables are the average values obtained from testing duplicate specimens but when there was a large variation in results of these duplicate specimens a third specimen was subjected to the same treatment and the average taken from the two giving most similar values.

The first eight heats, with the exception of heat No. 1, belong to classes of alloy steels that were not thoroughly investigated because the first heats tested showed either lack of promise or because a more complete investigation of the particular class was intended at some other time. This group of eight steels consists of heats of medium manganese, manganese-chromium-vanadium, titanium, manganese-silicon, and manganese-molybdenum. Four steels were made in which copper was added in sufficient quantities to have a marked influence on the mechanical properties. The two classes of steels that were most thoroughly investigated were nickel-manganese and nickel-manganese-vanadium alloys. These two classes have one point in common with the other steels in that manganese is present in sufficient quantity to be considered an alloy.[1]

[1]Albert Sauveur, "The Metallography and Heat Treatment of Iron and Steel," third edition, 1926, p. 335.

Table II
Carbon Steel—Heat Number 1

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
1A	22.0	34.5	41,600	81,400	8.0	As cast
1B	28.0	45.0	44,250	78,700	20.5	Annealed 1650 degrees Fahr.
1C	29.0	45.0	43,400	77,000	....	Annealed 1700 degrees Fahr.
1D	29.5	48.0	46,750	77,250	....	Double annealed 1650-1650 degrees Fahr.
1E	29.5	47.0	45,000	77,200	22 to 28	Double annealed 1650-1525 degrees Fahr.
1F	30.5	50.0	40,750	76,000	....	Double annealed 1700-1500 degrees Fahr.
1G	30.0	47.0	50,700	79,000	....	Normalized 1700 degrees—Annealed 1525 degrees Fahr.
1H	31.0	47.0	45,000	79,000	34.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
1J	32.0	53.0	49,400	79,600	41.0	Double normalized 1650-1650 degrees — Tempered 1200 degrees Fahr.
1K	31.0	56.0	44,500	76,000	33.0	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.
1L	32.0	53.5	45,250	78,250	27.0	Normalized from 1650 degrees—Tempered 1325 degrees Fahr.
1M	27.0	57.0	60,500	90,750	46.0	Water-quenched 1650 degrees—Tempered 1250 degrees Fahr.
1N	30.0	58.5	48,750	74,000	37.0	Water-quenched 1650 degrees—Tempered 1325 degrees Fahr.

A Simple Carbon Steel

A carbon steel was made particularly to show the maximum elongation that could be expected from any steel of similar carbon content and also to use the results for a basis of comparing the effects of different alloy additions and different heat treatments. Considerable difficulty was encountered in making a carbon steel free from any alloy contamination. Even though the scrap was carefully selected it was necessary to make several heats before a steel was obtained that was practically free from nickel and copper. A carbon content of 0.30 per cent was specified because that was the approximate carbon content desired in most of the alloy steels. As to treatment, results given in Table II show that there is little difference in the effect of different treatments, with the exception of liquid quenching. Normalizing followed by either tempering or annealing increases the yield point slightly above that obtained by any annealing treatment, and normalizing and tempering also gives

Table III
Medium Manganese Steel—Heat Number 2

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
2A	14.5	37.0	88,000	102,500	14.0	As cast
2B	23.5	50.0	62,250	94,250	19.0	Annealed 1650 degrees Fahr.
2C	24.5	51.0	65,000	94,250	....	Annealed 1700 degrees Fahr.
2D	25.0	53.0	65,750	96,500	....	Double annealed 1650-1650 degrees Fahr.
2E	21.0	40.0	66,000	94,000	37.0	Double annealed 1650-1525 degrees Fahr.
2F	25.0	52.5	63,000	94,500	....	Double annealed 1700-1500 degrees Fahr.
2G	23.5	50.0	67,500	99,000	....	Normalized 1700 degrees — Annealed 1525 degrees Fahr.
2H	26.0	58.0	65,300	86,400	24.0	Normalized 1650 degrees — Tempered 1200 degrees Fahr.
2J	26.5	57.0	61,300	87,200	38.0	Double normalized 1650 — Tempered 1200 degrees Fahr.
2K	23.5	36.5	69,750	113,000	14.0	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.

highest impact values. Examination at high magnification of this steel after normalizing shows the structure to be almost entirely pearlitic. This would indicate that the spheroidizing treatment, treatment K, was not effective as spheroidization is promoted by first making the steel sorbitic.[2] This particular heat was subjected to liquid quenching more to show the effect of that treatment on the microstructure than to show the superior properties obtained as, usually, ship castings are of such shape and section that liquid quenching is out of the question.

Medium Manganese Steels

The mechanical properties of two steels containing more than 2.00 per cent manganese are given in Tables III and IV. Of the two steels the one containing approximately 2.00 per cent manganese has better static properties and decidedly better impact properties, even though this steel contains six points more carbon than the 2.25 per cent manganese steel. This would indicate that more than 2.00 per cent manganese in steels of this class is detrimental

[2]Albert Sauveur, "The Metallography and Heat Treatment of Iron and Steel," third edition, 1926, p. 285.

Table IV
Medium Manganese Steel—Heat Number 3

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
3A	12.5	17.0	68,250	105,000	15.0	As cast
3B	26.0	57.5	64,000	93,000	38.0	Annealed 1650 degrees Fahr.
3C	26.0	54.0	62,250	92,500	....	Annealed 1700 degrees Fahr.
3D	29.0	58.0	67,000	94,000	....	Double annealed 1650-1650 degrees Fahr.
3E	27.5	56.0	69,500	91,250	55.0	Double annealed 1650-1525 degrees Fahr.
3F	27.5	52.0	69,750	91,500	....	Double annealed 1700-1500 degrees Fahr.
3G	26.0	55.0	71,250	96,000	....	Normalized 1700 degrees—Annealed 1525 degrees Fahr.
3H	27.0	59.0	66,670	87,370	28.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
3J	28.0	59.0	69,000	85,750	48.0	Double normalized 1650-1650—Tempered 1200 degrees Fahr.
3K	25.0	59.0	56,750	98,750	35.0	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.

Table V
Manganese-Chromium-Vanadium Steel—Heat Number 4

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
4A	4.0	3.7	70,000	104,750	3.0	As cast
4B	22.5	48.0	62,500	104,100	11.0	Annealed 1650 degrees Fahr.
4C	23.0	49.0	61,500	104,000	....	Annealed 1700 degrees Fahr.
4D	23.5	50.0	70,000	105,600	....	Double annealed 1650-1650 degrees Fahr.
4E	23.5	46.0	68,000	100,000	22.0	Double annealed 1650-1525 degrees Fahr.
4F	24.0	48.0	62,250	101,500	....	Double annealed 1700-1500 degrees Fahr.
4G	23.0	47.0	75,000	103,500	....	Normalized 1700 degrees—Annealed 1525 degrees Fahr.
4H	16.0	41.5	86,750	112,250	7.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
4J	25.0	54.0	72,000	98,000	44.0	Double normalized 1650-1650—Tempered 1200 degrees Fahr.
4K	26.5	50.0	70,270	89,250	56.0	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.

to both ductility and resilience. It is necessary to have a comparatively high manganese content to obtain high strength and ductil-

Table VI

Titanium Steel—Heat Number 5

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
5A	....	....	.....	70,000	2.0	As cast
5B	21.5	35.0	55,500	92,000	11.0	Annealed 1650 degrees Fahr.
5C	22.5	37.0	54,000	89,750	....	Annealed 1700 degrees Fahr.
5D	24.0	37.0	60,000	90,000	....	Double annealed 1650-1650 degrees Fahr.
5E	24.0	39.0	57,500	90,000	12 to 21	Double annealed 1650-1525 degrees Fahr.
5F	23.5	36.0	52,100	87,500	....	Double annealed 1700-1500 degrees Fahr.
5G	24.0	37.0	66,250	91,600	....	Normalized 1650 degrees—Annealed 1525 degrees Fahr.
5H	24.5	40.5	56,000	90,750	21.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
5J	25.0	40.0	62,000	91,100	28.0	Double normalized 1650-1650—Tempered 1200 degrees Fahr.
5K	25.0	44.0	56,000	88,250	19 to 26	Normalized 1700-1525 degrees—Tempered 1300 degrees Fahr.

ity.[3] This is shown by Lorig and Williams[4] who have assembled the work of several investigators to show the effect of increase in carbon and in manganese on the mechanical properties. These properties compare favorably with properties of some of the more complex alloy steels, but the undesirable properties of medium manganese steel[5] make it unsuitable for use in large and intricate castings, particularly if the castings are to be annealed.[6]

Manganese-Chromium-Vanadium Steels

The results given in Table V show the ratio of yield point to tensile strength to be rather low for this steel in the annealed condition. Double annealing improves the static properties very little but does improve the resistance to impact. Normalizing followed

[3]H. S. Rawdon and F. Sillers, "Effect of Manganese on the Structure of Alloys of the Iron Carbon System." Scientific Paper of Bureau of Standards No. 464, 1923.

[4]C. H. Lorig and C. E. Williams, "Physical and Mechanical Properties of Some Well Known Cast Steels," *Symposium on Steel Castings*, 1932, p. 106. American Foundrymen's Association and American Society for Testing Materials.

[5]W. C. Hamilton, "Addition of Vanadium Improves Properties of Medium Manganese Steel," *Iron Age*, Vol. 129, 1932, p. 546.

[6]Fred Grotts, "Representative Properties of Cast Medium Pearlitic Steels," *Symposium on Steel Castings*, 1932, p. 169. The American Foundrymen's Association and The American Society for Testing Materials.

Table VII
Manganese-Silicon Steel—Heat Number 6

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
6A	20.5	27.0	57,750	89,750	3.5	As cast
6B	28.0	52.0	58,750	89,250	23.5	Annealed 1650 degrees Fahr.
6C	29.0	53.5	58,800	89,750	....	Annealed 1700 degrees Fahr.
6D	29.5	52.0	57,850	88,350	....	Double annealed 1650-1650 degrees Fahr.
6E	30.0	53.0	60,000	90,000	45.0	Double annealed 1650-1525 degrees Fahr.
6F	29.5	54.0	52,500	87,500	....	Double annealed 1700-1500 degrees Fahr.
6G	29.5	53.0	55,250	87,750	....	Normalized 1700 degrees Fahr.—Annealed 1525 degrees Fahr.
6H	29.0	56.0	57,500	89,100	23.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
6J	30.0	57.5	56,250	90,500	46.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
6K	31.5	61.5	53,800	83,500	36.5	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table VIII
Manganese-Silicon Steel—Heat Number 7

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
7A	24.0	44.0	53,250	89,750	14.5	As cast
7B	35.5	70.0	52,000	77,900	53.0	Annealed 1650 degrees Fahr.
7C	36.0	68.0	52,000	77,900	....	Annealed 1700 degrees Fahr.
7D	34.0	64.0	45,750	74,750	....	Double annealed 1650-1650 degrees Fahr.
7E	38.0	71.0	50,750	79,000	85.0	Double annealed 1650-1525 degrees Fahr.
7F	36.0	70.5	52,200	79,250	....	Double annealed 1700-1500 degrees Fahr.
7G	35.5	69.5	52,600	79,250	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
7H	35.0	70.5	53,750	79,500	51.5	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
7J	32.5	69.0	53,500	81,100	51.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
7K	36.0	72.0	50,500	77,100	45 to 76	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table IX
Manganese-Silicon Steel—Heat Number 8

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
8A	7.0	7.0	76,500	108,000	3.5	As cast
8B	26.0	42.0	58,750	94,000	16.0	Annealed 1650 degrees Fahr.
8C	25.5	41.0	57,600	93,200	....	Annealed 1700 degrees Fahr.
8D	27.0	47.0	64,000	93,400	....	Double annealed 1650-1650 degrees Fahr.
8E	27.0	43.0	59,500	93,100	21 to 28	Double annealed 1650-1525 degrees Fahr.
8F	26.0	47.0	57,400	92,500	....	Double annealed 1700-1500 degrees Fahr.
8G	27.0	47.0	69,000	95,000	....	Normalized 1650 degrees—Annealed 1525 degrees Fahr.
8H	26.5	49.5	61,250	94,400	20.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
8J	27.0	47.0	65,600	95,250	33.0	Double normalized 1650-1650 degrees — Tempered 1200 degrees Fahr.
8K	29.0	53.0	57,000	90,000	25 to 31	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.

by annealing, and both single and double normalizing followed by tempering, increase the yield point. Good ductility is obtained only by double normalizing and tempering and by spheroidizing. This steel is too hard for ordinary use but it could be softened up by decreasing the alloy content, preferably the manganese. The properties of several steels of similar composition but higher in carbon content are reported by Critchett.[7]

Titanium Steels

Titanium is usually added to steels as a deoxidizer. As titanium does form a carbide[8] it was thought that possibly appreciable quantities of titanium present in the form of an alloy would improve the properties of cast steel. Several titanium-bearing steels were included in this investigation but the properties of only one steel are given. Investigation of other steels has not yet been completed. Unfortunately, the scrap used in making heat No. 5 contained both nickel and chromium and both show up in the final analysis; however, results given in Table VI show higher tensile

[7] J. H. Critchett, "Chromium in Steel Castings," *Transactions*, American Foundrymen's Association, Vol. XLI, 1933.

[8] William M. Thornton, Jr., "Titanium," first edition, 1927, p. 52, The Chemical Catalogue Company.

Table X
Copper-Bearing Steel—Heat Number 9

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
9A	17.0	23.0	65,750	96,250	8.0	As cast
9B	28.0	50.0	59,000	80,000	40.0	Annealed 1650 degrees Fahr.
9C	28.5	47.5	56,000	79,750	....	Annealed 1700 degrees Fahr.
9D	29.0	49.0	61,500	80,250	....	Double annealed 1650-1650 degrees Fahr.
9E	29.0	51.5	63,000	79,250	49.0	Double annealed 1650-1525 degrees Fahr.
9F	30.0	51.5	60,000	78,500	....	Double annealed 1700-1500 degrees Fahr.
9G	29.5	53.0	63,000	79,250	....	Normalized 1650 degrees—Annealed 1525 degrees Fahr.
9H	28.0	55.0	59,500	81,750	40.0	Normalized 1650 degrees—Tempered 1200 degrees Fahr.
9J	28.5	54.5	64,750	83,750	50.0	Double normalized 1650-1650 degrees Fahr.—Tempered 1200 degrees Fahr.
9K	31.0	57.0	61,000	76,500	49.0	Double normalized 1700-1525 degrees Fahr.—Tempered 1300 degrees Fahr.

Table XI
Manganese-Silicon-Copper Steel—Heat Number 10

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
10A	1.0	1.0	106,250	115,000	3.0	As cast
10B	30.5	60.0	61,250	86,500	10.0	Annealed 1650 degrees Fahr.
10C	30.5	58.0	59,750	83,500	....	Annealed 1700 degrees Fahr.
10D	31.5	61.5	61,500	86,500	....	Double annealed 1650-1650 degrees Fahr.
10E	30.0	65.5	61,000	88,250	21 to 58	Double annealed 1650-1525 degrees Fahr.
10F	31.0	61.0	56,000	86,000	....	Double annealed 1700-1500 degrees Fahr.
10G	32.0	67.0	60,250	88,500	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
10H	30.5	63.0	58,000	84,500	24.0	Normalized 1650 degrees degrees Fahr.—Tempered 1200 degrees Fahr.
10J	30.5	63.0	59,500	88,000	43.0	Double normalized 1650-1650 degrees Fahr.—Tempered 1200 degrees Fahr.
10K	32.0	66.5	56,000	83,250	33.0	Double normalized 1700-1525 degrees Fahr.—Tempered 1300 degrees Fahr.

strength and more brittleness than would be expected with a steel of similar analysis containing no titanium. Results indicate that titanium has a hardening and embrittling effect but as yet there are

insufficient data to form a basis of any definite conclusions. The titanium was added in the form of low carbon ferrotitanium, half in the furnace just before tapping, and half in the stream as the metal ran into the ladle. The recovery was approximately sixty per cent.

Manganese-Silicon Steels

Results of three manganese-silicon steels are given in Tables VII, VIII and IX. Heat No. 6 shows good ductility but the yield point is low and impact values only fair. Heat No. 7 is so low in carbon it would be impractical to use it for a casting alloy. Heat No. 8 has good strength and ductility but low yield point and particularly poor impact resistance for a steel of this ductility. Indications are that higher manganese, silicon, or carbon would make this type of steel so brittle it would be worthless. Apparently good mechanical properties can be obtained in the low carbon steels but as the carbon is raised brittleness increases at a much faster rate than the tensile strength. The properties of steels of this class do not equal those of medium manganese and there is no particular reason to believe that they are better casting steels. Possibly they are more fluid but any advantage in casting properties is more than offset by the poor dynamic properties of the steels of medium carbon content.

Copper-Bearing Steels

Heat No. 9 is a carbon steel to which 0.89 per cent copper has been added. Comparing the properties of this steel with those of the carbon steel, it will be observed that the copper steel has considerably higher yield point and impact properties. Heat No. 10 is so low in copper (0.35 per cent) it could be classed as a manganese-silicon steel were it not for the results showing a higher ratio of yield point to tensile strength than would be obtained in a manganese-silicon steel of similar analysis. Heat No. 11 is a nickel-manganese steel containing more than 1.00 per cent copper. Both static and impact properties are equal to those of the nickel-manganese steels higher in either or both, nickel and manganese. Results in Table XIII show the effect of adding 1.25 per cent copper to a 1.00 per cent manganese steel. This steel has excellent ductility and impact properties but the carbon is too low in a steel of this alloy content to obtain high strength. In all of these steels copper

Table XII
Nickel-Manganese-Copper Steel—Heat Number 11

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
11A	15.0	19.0	70,750	100,100	5.5	As cast
11B	25.0	40.0	69,100	96,350	34 to 42	Annealed 1650 degrees Fahr.
11C	26.0	48.0	66,500	94,850	....	Annealed 1700 degrees Fahr.
11D	26.0	48.0	66,000	93,000	....	Double annealed 1650-1650 degrees Fahr.
11E	26.5	51.0	72,750	96,750	47	Double annealed 1650-1525 degrees Fahr.
11F	27.0	50.5	67,400	93,100	....	Double annealed 1650-1500 degrees Fahr.
11G	26.5	48.5	70,750	94,500	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
11H	25.0	53.0	69,500	96,000	29 to 38	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
11J	25.0	52.0	73,300	95,000	43.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
11K	29.0	58.0	65,600	86,750	44 to 56	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XIII
Copper-Manganese Steel—Heat Number 12

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
12A	12.0	18.5	71,400	91,000	5.5	As cast
12B	25.0	43.0	59,000	83,500	40.0	Annealed 1650 degrees Fahr.
12C	27.5	49.0	59,000	82,600	....	Annealed 1700 degrees Fahr.
12D	29.0	52.0	61,750	82,000	....	Double annealed 1650-1650 degrees Fahr.
12E	30.0	51.0	63,750	83,350	58.0	Double annealed 1650-1525 degrees Fahr.
12F	29.5	54.0	57,000	81,250	....	Double annealed 1700-1500 degrees Fahr.
12G	27.5	47.0	62,750	81,750	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
12H	26.0	57.0	65,000	88,500	29 to 47	Normalized 1650 degrees Fahr. — Tempered 1200 degrees Fahr.
12J	25.0	57.0	72,750	87,250	62.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
12K	30.0	60.0	60,000	78,500	69.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

has the effect of raising the yield point but apparently has little or no effect on the tensile strength. Microscopic examination shows that copper comes out of solution when it is present in steel in quan-

Table XIV
Manganese-Molybdenum Steel—Heat Number 13

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
13A	14.0	33.0	68,750	103,750	18.0	As cast
13B	23.0	36.5	59,000	83,500	44.0	Annealed 1650 degrees Fahr.
13C	27.0	44.0	58,250	83,000	....	Annealed 1700 degrees Fahr.
13D	28.0	55.0	62,500	83,750	....	Double annealed 1650-1650 degrees Fahr.
13E	28.5	51.0	59,000	86,500	44.0	Double annealed 1650-1525 degrees Fahr.
13F	27.5	41.5	59,500	82,750	....	Double annealed 1700-1500 degrees Fahr.
13G	27.0	48.5	68,000	86,000	....	Normalized 1700 degrees Fahr. — Annealed 1525 degrees Fahr.
13H	27.5	58.0	63,000	86,850	43.0	Normalized 1650 degrees Fahr. — Tempered 1200 degrees Fahr.
13J	26.0	60.0	62,700	83,750	65.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
13K	26.0	52.5	64,500	83,500	65.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XV
Manganese-Molybdenum Steel—Heat Number 14

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
14A	7.0	6.0	76,250	113,000	....	As cast
14B	23.0	39.0	54,250	88,500	....	Annealed 1650 degrees Fahr.
14C	23.0	35.0	51,250	87,750	....	Annealed 1700 degrees Fahr.
14D	25.5	36.5	56,000	87,000	....	Double annealed 1650-1650 degrees Fahr.
14E	24.0	36.0	56,000	88,000	....	Double annealed 1650-1525 degrees Fahr.
14F	25.0	37.5	52,250	87,000	....	Double annealed 1700-1500 degrees Fahr.
14G	24.0	38.0	62,000	88,000	....	Normalized 1650 degrees Fahr. — Annealed 1525 degrees Fahr.
14H	23.5	48.5	65,500	93,750	28.0	Normalized 1650 degrees Fahr. — Tempered 1200 degrees Fahr.
14J	24.5	46.0	63,750	94,250	35.0	Double normalized 1650-1650 degrees — Tempered 1200 degrees Fahr.
14K	28.0	55.0	61,250	81,250	....	Double normalized 1700-1525 degrees — Tempered 1300 degrees Fahr.

tities somewhat above 0.34 per cent, unless the steel contains appreciable quantities of silicon or some other alloy that will cause the copper to be retained in solution. This copper segregation can be

Table XVI
Nickel Manganese Steel—Heat Number 15

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
15A	19.0	31.0	57,000	89,750	11.0	As cast
15B	27.0	56.0	61,250	91,000	42.0	Annealed 1650 degrees Fahr.
15C	28.0	57.0	56,300	87,000	....	Annealed 1700 degrees Fahr.
15D	29.0	56.0	62,000	88,750	....	Double annealed 1650-1650 degrees Fahr.
15E	27.5	53.0	61,000	91,000	50.0	Double annealed 1650-1525 degrees Fahr.
15F	29.0	56.0	62,600	89,200	....	Double annealed 1700-1500 degrees Fahr.
15G	28.0	53.5	67,000	90,100	....	Normalized 1650 degrees —Annealed 1525 degrees Fahr.
15H	27.5	55.0	62,300	86,400	46.0	Normalized 1650 degrees Fahr. — Tempered 1200 degrees Fahr.
15J	28.0	54.0	71,000	89,500	52.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
15K	20.0	45.0	60,250	97,500	35 to 50	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

noticed in risers and around the grains exposed by hot tears in copper-bearing steels. Possibly this copper segregation is a contributing cause to these hot tears in steel containing high copper, and until there is some conclusive evidence that copper not retained in solution does not cause castings to crack, copper steels will never be very popular with foundrymen.

Manganese-Molybdenum Steels

The two manganese-molybdenum steels contain slightly more than 0.30 per cent molybdenum but less manganese than is usually present in steels of this class.[9, 10] Heat No. 13 possesses good ductility and a high ratio of yield point to tensile strength, but the tensile strength is not particularly high. Heat No. 14, which contains 0.37 per cent carbon and 0.93 per cent manganese, does not show particularly good yield point and tensile strength for the carbon and alloy content. No doubt better strength would have been obtained if this heat were higher in manganese. Comparing results from these two steels with results obtained by other investigators,[9, 10] it is apparent that steels of this class should contain more than 1.00

[9]C. H. Lorig and C. E. Williams, "Physical and Mechanical Properties of Some Well-Known Cast Steels," *Symposium on Steel Castings*, 1932, p. 130. The American Foundrymen's Association and The American Society for Testing Materials.

[10]J. L. Gregg, "Alloys of Iron and Molybdenum," first edition, 1932, p. 406. McGraw Hill Book Company.

Table XVII

Nickel-Manganese-Molybdenum Steel—Heat Number 16

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
16A	12.0	22.0	86,600	111,100	4.5	As cast
16B	19.5	35.0	73,480	106,300	10.0	Annealed 1650 degrees Fahr.
16C	21.5	32.5	75,900	106,600	....	Annealed 1700 degrees Fahr.
16D	20.0	36.0	70,000	107,400	....	Double annealed 1650-1650 degrees Fahr.
16E	20.0	39.0	71,500	108,200	17.0	Double annealed 1650-1525 degrees Fahr.
16F	21.0	38.0	72,500	109,600	....	Double annealed 1700-1500 degrees Fahr.
16G	19.5	34.5	72,600	109,500	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
16H	21.0	46.5	77,000	102,750	30.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
16J	21.0	46.5	81,300	104,100	55.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
16K	18.0	44.0	62,200	101,300	23 to 37	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XVIII

Nickel Manganese Steel—Heat Number 17

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
17A	5.0	5.0	68,100	105,500	2.0	As cast
17B	22.0	39.0	63,500	105,500	17.0	Annealed 1650 degrees Fahr.
17C	23.5	43.5	62,000	104,500	....	Annealed 1700 degrees Fahr.
17D	23.5	44.5	65,200	104,000	....	Double annealed 1650-1650 degrees Fahr.
17E	25.5	45.0	67,750	106,000	27.5	Double annealed 1650-1525 degrees Fahr.
17F	24.0	45.0	66,000	102,750	....	Double annealed 1700-1500 degrees Fahr.
17G	25.0	46.0	69,150	102,400	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
17H	22.0	46.0	71,000	103,100	30.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
17J	24.0	48.0	74,500	100,100	47.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
17K	25.5	44.0	58,000	98,250	29 to 39	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

per cent manganese and over 0.25 per cent carbon to obtain the best combination of strength and ductility.

Nickel-Manganese Steels

If the normal manganese content is increased to 1.00 to 1.50

Table XIX
Nickel-Manganese Steel—Heat Number 18

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
18A	12.5	14.0	58,500	93,800	4.0	As cast
18B	28.0	57.0	58,250	88,100	48.0	Annealed 1650 degrees Fahr.
18C	28.5	57.0	57,000	87,500	....	Annealed 1700 degrees Fahr.
18D	29.0	56.0	62,000	88,200	....	Double annealed 1650-1650 degrees Fahr.
18E	28.0	53.5	62,500	89,100	70.0	Double annealed 1650-1525 degrees Fahr.
18F	29.0	55.0	59,900	87,750	....	Double annealed 1700-1500 degrees Fahr.
18G	29.5	57.0	66,250	88,400	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
18H	27.5	56.0	62,000	87,500	62 to 77	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
18J	29.0	58.5	70,100	86,200	6.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
18K	26.5	54.0	53,500	86,250	59.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XX
Nickel-Manganese Steel—Heat Number 19

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
19A	6.0	6.5	81,400	104,400	7 to 13	As cast
19B	24.5	45.5	62,900	100,000	15 to 54	Annealed 1650 degrees Fahr.
19C	28.0	54.0	61,100	97,250	....	Annealed 1700 degrees Fahr.
19D	24.0	45.5	66,000	100,000	....	Double annealed 1650-1650 degrees Fahr.
19E	25.0	46.0	66,500	100,750	40.0	Double annealed 1650-1525 degrees Fahr.
19F	26.0	49.0	62,000	95,000	....	Double annealed 1700-1500 degrees Fahr.
19G	26.5	53.0	67,750	96,000	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
19H	24.5	50.0	68,000	95,200	45.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
19J	25.0	53.0	73,750	94,000	57.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
19K	26.0	51.0	60,000	90,000	44.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

per cent in steels containing 1.00 to 2.00 per cent nickel, mechanical properties can be obtained which are comparable to those of straight nickel steels containing appreciably higher percentages of nickel. In this type of steel either the effect of nickel is intensified by the man-

Table XXI
Nickel-Manganese Steel—Heat Number 20

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
20A	2.0	1.5	72,500	85,000	2.0	As cast
20B	21.0	34.0	69,000	106,750	10.0	Annealed 1650 degrees Fahr.
20C	21.0	34.0	67,000	105,500	....	Annealed 1700 degrees Fahr.
20D	24.0	46.0	70,500	105,750	....	Double annealed 1650-1650 degrees Fahr.
20E	23.5	44.0	72,750	106,000	20.0	Double annealed 1650-1525 degrees Fahr.
20F	24.0	44.0	71,700	105,000	....	Double annealed 1700-1500 grees Fahr.
20G	23.0	38.0	73,000	108,500	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
20H	23.0	41.5	72,500	102,000	18 to 30	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
20J	21.5	36.5	73,500	101,000	21.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
20K	21.0	38.0	57,000	104,250	12.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XXII
Nickel-Manganese-Vanadium Steel—Heat Number 21

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
21A	3.5	3.5	94,370	104,370	3.0	As cast
21B	18.5	37.5	72,750	110,400	15.5	Annealed 1650 degrees Fahr.
21C	20.0	38.5	77,700	112,000	....	Annealed 1700 degrees Fahr.
21D	24.0	49.0	70,500	105,250	....	Double annealed 1650-1650 degrees Fahr.
21E	23.0	37.0	73,000	108,000	33.0	Double annealed 1650-1525 degrees Fahr.
21F	27.0	54.0	69,100	98,100	....	Double annealed 1700-1500 degrees Fahr.
21G	25.5	52.0	75,500	99,500	....	Normalized 1700 degrees Fahr.—Annealed 1525 degrees Fahr.
21H	18.0	45.5	87,750	107,000	10.5	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
21J	25.0	54.0	75,500	95,100	36.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
21K	21.5	44.5	57,000	97,000	38.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

ganese, or the undesirable properties of high manganese are counteracted by the nickel. The steels in this group were made to determine the effect of various percentages of carbon, manganese and nickel, with the carbon ranging from 0.15 per cent to 0.37 per cent,

Table XXIII
Nickel-Manganese-Vanadium Steel—Heat Number 22

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
22A	2.5	2.5	69,250	97,000	3.0	As cast
22B	24.0	47.0	62,250	97,500	18.0	Annealed 1650 degrees Fahr.
22C	24.0	44.5	61,750	95,500	....	Annealed 1700 degrees Fahr.
22D	24.0	46.5	74,750	98,000	....	Double annealed 1650-1650 degrees Fahr.
22E	24.5	51.0	65,750	97,250	28.0	Double annealed 1650-1525 degrees Fahr.
22F	26.0	49.0	66,500	92,000	....	Double annealed 1700-1500 degrees Fahr.
22G	25.0	47.0	73,750	95,750	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
22H	24.0	49.5	62,250	97,400	16.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
22J	26.0	54.0	70,600	95,500	45.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
22K	27.5	55.0	68,500	88,750	31 to 46	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

Table XXIV
Nickel-Manganese-Vanadium Steel—Heat Number 23

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
23A	3.0	3.5	106,250	128,250	2.5	As cast
23B	21.0	38.0	66,000	106,750	18.5	Annealed 1650 degrees Fahr.
23C	21.0	35.0	65,000	105,000	....	Annealed 1700 degrees Fahr.
23D	22.0	40.0	67,000	105,000	....	Double annealed 1650-1650 degrees Fahr.
23E	21.0	38.0	72,000	109,300	23.0	Double annealed 1650-1525 degrees Fahr.
23F	24.5	42.5	64,000	99,500	....	Double annealed 1700-1500 degrees Fahr.
23G	23.5	43.0	70,300	100,000	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
23H	27.5	35.0	81,500	115,000	15.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
23J	20.0	44.5	82,250	112,000	24.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
23K	26.0	49.5	68,700	90,750	46.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

manganese from 0.98 per cent to 1.44 per cent, and nickel from 1.12 to 2.32 per cent. Comparison of results in Tables XVI and XVII shows the higher carbon steel, heat No. 16, has higher strength but less ductility than the steel containing lower carbon and higher per-

Table XXV
Nickel-Manganese-Vanadium Steel—Heat Number 24

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
24A	12.0	29.5	91,100	115,000	14.0	As cast
24B	21.5	42.5	64,350	101,100	26.0	Annealed 1650 degrees Fahr.
24C	22.0	36.0	63,350	101,750	....	Annealed 1700 degrees Fahr.
24D	22.5	38.5	68,000	101,750	....	Double annealed 1650-1650 degrees Fahr.
24E	22.5	39.0	69,000	104,000	27.0	Double annealed 1650-1525 degrees Fahr.
24F	26.5	49.0	64,750	96,000	....	Double annealed 1700-1500 degrees Fahr.
24G	25.0	44.0	69,150	98,500	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
24H	20.0	49.5	91,000	112,000	30.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
24J	19.5	50.5	93,100	112,500	39.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
24K	27.0	56.0	64,000	90,000	71.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

centage of alloys, heat No. 15. Heat No. 17 has rather unusual properties in that it has better ductility and impact resistance than heat No. 16 even though the carbon and alloy content is higher in the more ductile steel. Heats No. 18 and 19 contain higher percentages of manganese than nickel. Both steels show good strength in addition to excellent ductility and good impact properties. Of the two, the steel lower in carbon content shows the better ratio of yield point to tensile strength. Heat No. 20 has excellent strength but ductility and impact properties are low due no doubt to the combination of 0.32 per cent carbon and 2.18 per cent nickel. Comparing the results of these steels with results of similar steels reported by Zima,[11] indication is that best results can be obtained with a range in analysis of: Carbon from 0.25 to 0.35 per cent, manganese 1.00 to 1.50 per cent, and nickel 1.00 to 2.00 per cent.

Nickel-Manganese-Vanadium Steels

This group consists of nickel-manganese steels of various analyses to which have been added small quantities of vanadium. The manganese content (1.47 per cent) of heat No. 21 is too high, as this high manganese in a medium carbon steel containing both nickel

[11]Albert G. Zima, "Properties and Uses of Some Cast Nickel Alloy Steels," *Transactions*, American Foundrymen's Association, Vol. XLI, 1933.

Table XXVI

Nickel-Manganese-Vanadium-Molybdenum Steel—Heat Number 25

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
25A	11.5	11.5	82,250	108,750	4.5	As cast
25B	26.5	53.0	63,750	94,350	39 to 53	Annealed 1650 degrees Fahr.
25C	25.5	52.0	62,000	94,000	....	Annealed 1700 degrees Fahr.
25D	25.0	51.5	67,250	96,000	....	Double annealed 1650-1650 degrees Fahr.
25E	25.0	48.0	67,750	98,400	52.0	Double annealed 1650-1525 degrees Fahr.
25F	28.0	56.5	64,500	93,000	....	Double annealed 1700-1500 degrees Fahr.
25G	26.0	52.0	70,300	95,000	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
25H	23.0	57.5	76,100	98,000	42.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
25J	24.0	58.0	76,500	96,000	69.0	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
25K	20.0	48.0	54,000	94,750	46.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

and vanadium makes the steel too hard; however, the steel does show a good ratio of yield point to tensile strength and good ductility for a steel of such high strength. Heat No. 22, which is almost as high in nickel and carbon, but with 0.50 per cent less manganese than heat No. 21, has good properties with exception of comparatively low resilience. In heat No. 23 the sum of nickel and carbon is considerably higher than was specified. The high tensile strength and high yield point of this steel is accompanied by comparatively low ductility. Poor ductility is characteristic of heat No. 24. This steel contains the lowest manganese content (0.88 per cent) of any heat of this group. Heat No. 25 contains 0.33 per cent molybdenum and a nickel content of over 2.00 per cent. Excellent mechanical properties are obtained from this steel but there are so many alloys present the cost of this steel would not be compensated by the improved properties, particularly when equally as good properties can be obtained in cheaper steels of simpler composition. Heat No. 26 has excellent static properties but is low in impact. This low impact may be due in part to 0.25 per cent chromium that was recovered from the charge. The dynamic properties of these nickel-manganese-vanadium steels are comparatively low, particularly in the annealed condition. However, when it is taken into consideration that most

Table XXVII
Nickel-Manganese-Vanadium Steel—Heat Number 26

Heat Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
26A	4.0	3.5	77,000	103,700	2.0	As cast
26B	23.0	44.0	67,500	102,750	15.0	Annealed 1650 degrees Fahr.
26C	22.0	43.0	66,000	102,100	....	Annealed 1700 degrees Fahr.
26D	25.0	46.0	70,750	101,500	....	Double annealed 1650-1650 degrees Fahr.
26E	25.0	50.0	71,750	100,400	30.0	Double annealed 1650-1525 degrees Fahr.
26F	25.5	47.0	72,000	99,200	....	Double annealed 1700-1500 degrees Fahr.
26F1	....	....	.....	.....	22.0	Double annealed 1800-1500 degrees Fahr.
26G	25.5	48.0	76,000	102,400	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
26H	24.5	51.0	73,250	102,750	21.0	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
26J	24.0	46.5	79,250	104,000	26.5	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
26K	27.0	52.0	71,000	93,400	23.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.
26L	26.0	49.0	73,750	100,250	55.0	Normalized 1650 degrees Fahr.—Tempered 1325 degrees Fahr.—furnace-cooled
26M	19.5	48.0	101,750	115,000	52.0	Water quench 1650 degrees Fahr.—Tempered 1250 degrees Fahr.
26N	25.0	50.0	80,500	104,250	38.0	Water quench 1650 degrees Fahr.—Tempered 1325 degrees Fahr.—Furnace-cooled

of these steels are comparatively high in carbon, the impact resistance compares favorably with that of other steels of equal strength. Better impact properties are reported by Strauss.[12] Several steels of this class were made with a vanadium range of 0.25 per cent to 0.50 per cent. These steels were exceedingly hard and brittle and would not react satisfactorily to heat treatment. Indications are that best results can be obtained if the vanadium content is limited to somewhat less than 0.15 per cent, and that the nickel and manganese content is slightly lower than in a nickel-manganese steel which contains no vanadium. The properties of three steels containing less than 0.30 per cent carbon and various amounts of manganese, nickel and vanadium are reported by Strauss.[12]

[12]Jerome Strauss, "Vanadium in Steel Castings," *Transactions*, American Foundrymen's Association, Vol. XLI, 1933.

Table XXVIII
Treatment B

Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
1B	28.0	45.0	44,250	78,700	20.5	
2B	23.5	50.0	62,250	94,250	19.0	
3B	26.0	57.5	64,000	93,000	38.0	
4B	22.5	48.0	62,500	104,100	11.0	
5B	21.5	35.0	55,500	92,000	11.0	
6B	28.0	52.0	58,750	89,250	23.5	
7B	35.5	70.0	52,000	77,900	53.0	
8B	26.0	42.0	58,750	94,000	16.0	
9B	28.0	50.0	59,000	80,000	40.0	
10B	30.5	60.0	61,250	86,500	10.0	
11B	25.0	40.0	69,100	96,350	34 to 42	Annealed 1650 degrees Fahr.
12B	25.0	43.0	59,000	83,500	40.0	
13B	23.0	36.5	59,000	83,500	44.0	(900 degrees Cent.)
14B	23.0	39.0	54,250	88,500	....	
15B	27.0	56.0	61,250	91,000	42.0	
16B	19.5	35.0	73,480	106,300	10.0	
17B	22.0	39.0	63,500	105,100	17.0	
18B	28.0	57.0	58,250	88,100	48.0	
19B	24.5	45.5	62,900	100,000	15 to 34	
20B	21.0	34.0	69,000	106,750	10.0	
21B	18.5	37.5	72,750	110,400	15.5	
22B	24.0	47.0	62,250	97,500	18.0	
23B	21.0	38.0	66,000	106,750	18.5	
24B	21.5	42.5	64,750	101,100	26.0	
25B	26.5	53.0	63,750	94,350	39 to 53	
26B	23.0	44.0	67,500	102,750	15.0	

Heat Treatment

Comparison of the properties of different steels subjected to the same treatment can be made most easily by observing the results given in Tables XXVIII, XXIX, and XXX, but a comparison of the effects of different treatments on each steel can better be made from the results given in Tables II to XXVII inclusive. To show the general effect of different treatments the results obtained from all heats were averaged for each treatment and listed in Table XXXI. The relation of difference in properties due to different treatments may vary slightly in different steels but as a rule the same relation that holds for any specific steel is shown in the average values. Ductility in the untreated steels usually is inversely proportional to the percentages of carbon and alloys present. This is recognized when it is considered that the elongation of the 0.30 per cent carbon steel is higher than that of any other steel except heat No. 9, which heat contained only 0.09 per cent carbon. For ductility in the untreated specimens is shown in the heats containing approximately 1.00 per cent copper and in the heats that contain molybdenum.

The difference in results from annealing at 1650 degrees Fahr. (900 degrees Cent.) and at 1700 degrees Fahr. (925 degrees Cent.)

Table XXIX

Treatment E

Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Sq. In.	Tensile Strength Pounds Per Sq. In.	Izod Foot Pounds	Treatment
1E	29.0	47.0	45,000	77,200	25 to 28	
2E	21.0	40.0	66,000	94,000	37.0	
3E	27.5	56.0	69,500	91,250	55.0	
4E	23.5	46.0	68,000	100,000	22.0	
5E	24.0	39.0	57,500	90,000	12 to 21	
6E	30.0	53.0	60,000	90,000	45.0	
7E	38.0	71.0	50,750	79,000	85.0	
8E	27.0	43.0	59,500	93,100	21 to 28	
9E	29.0	51.5	63,000	79,250	49.0	
10E	30.0	65.5	61,000	88,250	21 to 58	Annealed 1650 degrees Fahr.
11E	26.5	51.0	72,750	96,750	47.0	
12E	30.0	51.0	63,750	83,350	58.0	followed by anneal at 1525
13E	28.5	51.0	59,000	86,500	44.0	
14E	24.0	36.0	56,000	88,000	....	degrees Fahr. (900 and 830
15E	27.5	53.0	61,000	91,000	50.0	
16E	20.0	39.0	71,500	108,200	17.0	degrees Cent.)
17E	25.5	45.0	67,750	106,000	27.5	
18E	28.0	63.5	62,500	89,100	70.0	
19E	25.0	46.0	66,500	100,750	40.0	
20E	23.5	44.0	72,750	106,000	20.0	
21E	23.0	37.0	73,000	108,000	33.0	
22E	24.5	51.0	65,750	97,250	28.0	
23E	21.0	38.0	72,000	109,300	23.0	
24E	22.5	39.0	69,000	104,000	27.0	
25E	25.0	48.0	67,750	98,400	52.0	
26E	25.5	50.0	71,750	100,400	30.0	

is that the higher temperature gives slightly better elongation with a corresponding decrease in yield point and tensile strength. Double annealing increases the yield point and elongation and has a very marked effect in improving the impact properties obtained on single annealing. For the three double annealing treatments, D. E and F, highest ductility and lowest tensile strength resulted from treatment F, which treatment consisted of annealing at 1700 degrees Fahr. (925 degrees Cent.) for the initial treatment followed by annealing at 1500 degrees Fahr. (815 degrees Cent.), the latter temperature being only slightly above the critical range for most of the steels.

Almost without exception, normalizing followed by annealing increased the yield point and gave ductility values approximately equal to the best obtained by any annealing treatment. Unfortunately, data showing the effect of this treatment on impact properties were not obtained.

Single or double normalizing followed by tempering increased the yield point and reduction of area. Single normalizing and tempering usually gave slightly less elongation than was obtained by annealing. Double normalizing and tempering gave elongation slight-

Table XXX

Treatment J

Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
1J	32.0	53.0	49,400	79,600	41.0	
2J	26.5	57.0	61,300	87,200	38.0	
3J	28.0	59.0	69,000	85,750	48.0	
4J	25.0	54.0	72,000	98,000	44.0	
5J	25.0	40.0	62,000	91,100	28.0	
6J	30.0	57.5	56,250	90,500	46.0	
7J	32.5	69.0	53,500	81,100	51.0	
8J	27.0	47.0	65,600	95,250	33.0	
9J	28.5	54.5	64,750	83,750	50.0	Double normalized 1650-1650
10J	30.5	63.0	59,500	88,000	43.0	
11J	25.0	52.0	73,300	95,000	43.0	degrees Fahr. (900-900 de-
12J	25.0	57.0	72,750	87,250	62.0	
13J	26.0	60.0	62,700	83,750	65.0	grees Cent.) — Tempered
14J	24.5	46.0	63,750	94,250	35.0	
15J	28.0	54.0	71,000	89,500	52.0	1200 degrees Fahr. (650
16J	21.0	46.5	81,300	104,100	55.0	
17J	24.0	48.0	74,500	100,100	47.0	degrees Cent.)
18J	29.0	58.5	70,100	86,200	61.0	
19J	25.0	53.0	73,750	94,000	57.0	
20J	21.5	36.5	73,500	101,000	21.0	
21J	25.0	54.0	75,500	95,100	36.0	
22J	26.0	54.0	70,600	95,500	45.0	
23J	20.0	44.5	82,250	112,000	24.0	
24J	19.5	50.5	93,100	112,500	39.0	
25J	24.0	58.0	76,500	96,000	69.0	
26J	24.0	46.5	79,250	104,000	26.5	

ly less than obtained by double annealing but the reduction of area, yield point, and impact properties were higher than obtained with any other treatment. One of the advantages of a normalizing and tempering treatment is that if certain physical specifications are within narrow limits the tempering temperature can be varied to compensate for slight variations in analyses.

Treatment K was intended for a spheroidizing treatment but the time of holding at the tempering or spheroidizing temperature was not sufficient to effect complete transformation. Spheroidizing increases the ductility but generally it causes a big drop in both yield point and tensile strength, but to obtain full advantage of the treatment the steel must be subjected to the spheroidizing temperature for a long period. A specific application for this treatment is in raising the ductility of hard steels.

The Effect of Treatments on the Structure

Photomicrographs were made of the carbon steel, heat No. 1, and of one alloy steel, heat No. 26, to show the effect of each treatment on the structure. Little difference could be observed in the

Table XXXI
Averages

Treatment Number	Per Cent Elongation	Per Cent Reduction of Area	Yield Point Pounds Per Square Inch	Tensile Strength Pounds Per Square Inch	Izod Foot Pounds	Treatment
A	10.1	15.5	74,190	100,650	6.6	As cast
B	24.7	46.0	61,730	94,290	27.3	Annealed 1650 degrees Fahr.
C	25.5	46.4	60,780	93,400	....	Annealed 1700 degrees Fahr.
D	26.3	48.7	63,860	93,730	....	Double annealed 1650-1650 degrees Fahr.
E	26.1	48.3	64,350	94,430	38.6	Double annealed 1650-1525 degrees Fahr.
F	27.0	49.7	61,560	91,770	....	Double annealed 1700-1500 degrees Fahr.
G	26.4	49.1	67,120	93,660	....	Normalized 1650 degrees Fahr.—Annealed 1525 degrees Fahr.
H	24.9	51.5	67,590	95,590	31.5	Normalized 1650 degrees Fahr.—Tempered 1200 degrees Fahr.
J	25.9	52.8	69,500	93,480	44.6	Double normalized 1650-1650 degrees Fahr. — Tempered 1200 degrees Fahr.
K	26.2	52.4	60,090	89,920	36.0	Double normalized 1700-1525 degrees Fahr. — Tempered 1300 degrees Fahr.

structures resulting from annealing at 1650 degrees Fahr. (900 degrees Cent.) and 1700 degrees Fahr. (925 degrees Cent.). Dendritic structures were noticeable in both steels after being subjected to either treatment. Double annealing caused a smaller grain size but dendritic structure was as much in evidence as with single annealing. Normalizing followed by annealing gave a structure similar to that obtained by double annealing. Normalizing followed by tempering gave a fine grain structure with good dispersion of constituents, practically free from dendrites. Double normalizing and tempering gave a structure similar to that obtained by single normalizing except that the grain size was smaller with the double treatment. Elimination of dendritic structure in cast steel apparently depends upon the cooling rate through the critical range and not upon the temperature of treatment. This is by no means a new idea as the work of Hall, Nissen and Taylor[18] conducted a number of years ago shows similar results. Even though dendritic structure can be eliminated by rapid cooling through the critical range, there will be a recurrence of this structure if the steel is heated to within or above the critical range and slowly cooled.

[18]John H. Hall, Arvid E. Nissen, and Knox Taylor, "Heat Treatment of Cast Steels," Bulletin, American Institute of Mining and Metallurgical Engineers, No. 153, 1919, p. 2888.

Summary

The results show that excellent mechanical properties can be obtained from cast steels comparatively low in alloy content providing the manganese content is above 1.00 per cent. Excellent results were obtained from several copper-bearing steels containing small quantities of other alloys. The most consistent results were obtained from nickel-manganese steels. Variations in carbon and alloy content do not appear to affect the properties of this class of steel as greatly as experienced with some other alloy steels. The highest strength for the quantities of carbon and alloys present was obtained in the nickel-manganese-vanadium steels. The molybdenum steels showed better resistance to impact than any of the high strength steels, and the copper steels possessed the best ductility in the as-cast state.

Better mechanical properties resulted from double treatments. The highest results, for all steels, excepting those low in carbon, were obtained by double normalizing and tempering. This treatment gives a high ratio of yield point to tensile strength, high dynamic properties and elongation approximately as high as obtained by double annealing.

Dendritic structure appears to be eliminated in cast steels only by comparatively rapid cooling through the critical range. Reheating to within or above the critical range followed by slow cooling will cause recurrence of dendritic structure even though the steel has previously been rapidly cooled from above the critical range. The results of normalizing are reflected in much finer grain and better dispersion of constituents than obtained by any annealing treatment. Double normalizing promotes even smaller grain size and better dispersion than obtained by single normalizing. Normalizing treatments must be followed by tempering to obtain good ductility unless the steel is low in carbon and alloys.

DISCUSSION

Written Discussion: By C. H. Lorig, Battelle Memorial Institute, Columbus, Ohio.

On reading this paper one is impressed with the magnitude and excellence of the investigation. With a subject as comprehensive as cast alloy steels for discussion it is reasonable that assertions somewhat adverse to general opinion and to fact may sometimes be found. One of them in this paper is, in particular, a serious indictment on a steel which, however, is of excellent quality as its properties show. It refers to the statements appearing on page 298 and 299 that

"copper segregation can be noticed in risers and around the grains exposed by hot tears in copper-bearing steels," and, that "possibly this copper segregation is a contributing cause to these hot tears in steel containing high copper, and until there is some conclusive evidence that copper does not cause castings to crack, copper steels will never be very popular with foundrymen."

Segregation of copper in steel is not as prevalent as might be concluded from the author's statement. The diagram for the copper-iron system, accompanying this discussion, shows a solubility of copper in gamma iron and in alpha iron at 810 degrees Cent. (1490 degrees Fahr.) to be 5.5 and 3.4 per cent respectively. The fact that the alloy may contain carbon is unimportant.[1] As normally copper steels for castings contain less than 5 per cent copper, they solidify with no separation and little if any segregation of copper. The work of the Committee on Heterogeneity of Steel Ingots[2] shows that even in large ingots containing as high as 1.2 per cent of copper practically no segregation was observed.

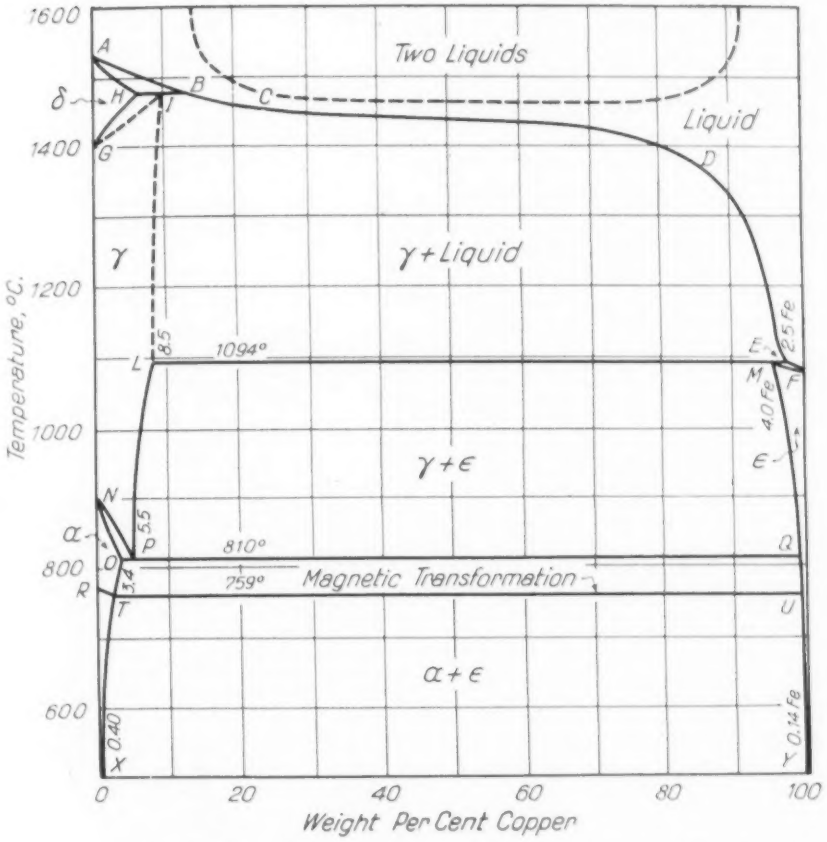
The decrease in solubility of copper in alpha iron from 810 degrees Cent. (1490 degrees Fahr.) to room temperature allows copper to separate uniformly as tiny particles, sometimes visible under the microscope, throughout the matrix of the steel. These particles do not concentrate at the grain boundaries nor do they migrate to form large globules of copper, but instead they remain as particles that may grow, with slow cooling or prolonged heating, to such size they barely become visible at a magnification of 100 diameters. The limiting solubility of copper at room temperature is probably between 0.4 and 0.5 per cent. Incidentally, the decreased solubility of copper with lowering temperatures permits the steels to be materially hardened and strengthened through the agency of precipitation hardening. Seemingly, the precipitation of copper from alpha iron as a result of this precipitation hardening treatment and otherwise is not a detriment to the steel nor is it a cause for segregation determinable by chemical or visual examination.

The alleged segregation noticed in risers and around the grains exposed by hot tears in copper-bearing steels is undoubtedly not a case of segregation at all, if the copper was alloyed with the steel early enough to melt and permit thorough distribution in the bath, but is the result of preferential oxidation of iron occurring in copper-iron alloys. Because the iron is oxidized in preference to copper, a heated surface of copper-steel exposed to air or other oxidizable gases will often have a copper-colored surface beneath the oxide scale. Such copper-colored surfaces were noticed frequently on tops of gates and risers from steel castings. While at first the inference might be made that the copper had *segregated* to the surface, closer examination will reveal the cause for the presence of copper to be that as stated above. Furthermore, with the specific gravity of copper at 8.9 and that of iron at 7.8, separation or segregation of copper in steel would tend to concentrate the copper toward the bottom of the casting, but this is not the case.

A similar explanation, that of preferred oxidation of iron, will account for the presence of copper at the grains exposed at hot tears of copper steels.

[1]Torajiro Ishiwara, Takeo Yonekura, and Toyozo Ishigaki, "On the Ternary Diagram of the System Iron, Carbon, and Copper," *Science Reports*, Tohoku Imperial University, Series I, Vol. 15, 1926, No. 1, p. 81-114.

[2]British Iron and Steel Institute, Fourth Report of the Heterogeneity of Steel Ingots, Advance copy, p. 51, 1932.



Equilibrium Diagram of the System Iron-Copper Showing the Limiting Solubilities of Copper in Iron. (From unpublished work of C. S. Smith)

Because of this fact it is not surprising that copper has been considered as a cause for hot tears in steel castings, whereas its presence in visible form is merely a consequence of the oxidized surface. In other words, the copper does not appear visually at the surface of hot tears until after the tears have formed. The accusation that copper causes cracking in cast steels is not founded on facts, consequently it should not detract from the popularity of copper steels where they could be used for castings.

Written Discussion: By A. Finlayson, metallurgist, Pacific Car and Foundry Co., Seattle, Washington.

The writer has studied this paper by Mr. Armstrong with a great deal of interest, and particularly that portion which discusses the effect of copper in steel castings.

We have been investigating the properties of copper steel alloys for many years and while Mr. Armstrong's report very closely corroborates results which we have obtained with similar compositions, we do not believe that the four heats which he discusses are sufficiently comprehensive for the deduction of any general conclusions as to the merits or demerits of copper as an alloying element in cast steel.

Furthermore, in seeking a steel for ship castings with high elastic and ductile properties, he seems to have entirely overlooked the aging, or precipitation hardening phenomenon so characteristic of copper steels.

Mr. Armstrong has very pertinently observed that copper is not retained in solid solution in quantities much over 0.35 per cent "unless the steel contains appreciable quantities of silicon or some other alloy that will cause the copper to be retained in solution," yet he does not show that he has investigated any high silicon steel with more than this percentage (0.34 per cent) of copper.

We have found that it requires more than the usual amounts of both silicon and manganese together with low carbon, (less than 0.20 per cent) in order to retain beneficial amounts of copper in solid solution. With such an arrangement, however, exceptional results may be obtained. In Heat No. 10, Mr. Armstrong unfortunately has included no more copper than it is stated would ordinarily be soluble without such high percentages of these two elements. This heat, therefore, proves nothing with respect to copper, except what is commonly known that even small amounts tend to raise the yield point.

The writer would like to submit the properties of three typical copper steels of which our foundry has made several hundred tons for commercial castings. It will be noted that these steels are all in the annealed condition and except for the higher copper content are of the same general composition as Mr. Armstrong's Heat No. 10. For ease of comparison, we have placed this heat, (No. 10B) in the first column:

	Armstrong's Heat No. 10 Annealed 900° C.	PC&F No. 1 Annealed 920° C. 2 Hrs.	PC&F No. 2 Annealed 900° C. 2 Hrs.	PC&F No. 3 Annealed 900° C. 2 Hrs.
Carbon	0.147	0.134	0.153	0.198
Manganese	1.43	1.29	1.08	1.16
Silicon	1.09	0.910	1.09	0.700
Copper	0.340	1.85	1.89	1.75
Yield Point, p.s.i.	61,250	68,350	69,550	80,000
Tensile strength, p.s.i.	86,500	90,000	89,750	93,500
Elongation in 2", per cent	30.50	32.80	29.75	23.50
Reduction of Area, per cent	60.00	59.30	57.25	41.50

With reference to the mention of "hot tears," and the belief that copper causes steel castings containing high copper to crack, we have found from long experience that there is no foundation whatever for this traditional idea unless by "high copper" is meant percentages in excess of 2.50. It is possible that with the compositions employed in Mr. Armstrong's experiments there might be a tendency to crack due to the fact that, with the exception of Heat No. 10 (which is admittedly not a copper steel), there is an excess of carbon and an insufficient amount of manganese and silicon to retain all of the copper in solid solution. Yet we doubt if this may be well demonstrated with single heats of only 1200 pounds. But even with similar composition, we have never encountered any greater degree of cracking than is met with in ordinary foundry practice although we have not made a sufficient quantity nor variety of castings in this category to warrant conclusive judgment.

With the compositions shown above, however, we may speak with some authority, since, over the past six years our foundry has poured several hundred tons of such steel into commercial castings ranging in weight from three pounds to seven tons, and made in heats of 3- to 10-ton charge. The castings have

ranged in sections from ¼ to 17 inches (the latter being cast shafting) yet we have never encountered any problem from cracks or hot tears. Indeed, we feel that we have much less difficulty in this regard than with high carbon and other types of alloy steels. Light section castings never crack; heavy sections rarely; and when the latter does occur it can generally be traced to faulty design.

Written Discussion: By Albert G. Zima, International Nickel Co., New York City.

In studying Mr. Armstrong's paper, the writer was especially interested in the results shown in Tables XIX and XX, dealing with the pearlitic nickel-manganese steels containing 1.00 to 1.25 per cent nickel.

In the opening paragraph of the paper, reference is made to the cracking of green or unannealed castings. From our observation of these steels, it appears that less trouble of this sort is encountered when the manganese range is held at about 1.00 to 1.30 per cent.

Likewise, it appears that with these low nickel steels, the best balance of tensile strength and ductility is obtained with the manganese held to about these same limits. The following data, obtained from a series of heats made in a 3-ton acid electric furnace, illustrate this point:

Chemical Composition

Heat Designation	Carbon	Nickel	Manganese	Silicon	Sulphur	Phosphorus
"A"	0.31	1.31	1.33	0.39	0.032	0.028
"B"	0.33	1.29	1.02	0.31	0.034	0.032
"C"	0.31	1.22	1.17	0.37	0.033	0.033
"D"	0.28	1.14	0.88	0.41	0.038	0.036
"E"	0.30	1.10	1.20	0.44	0.031	0.033

Mechanical Properties

After heat treating as follows:
Normalized at 1600 degrees Fahr., for two hours—tempered at 1200 degrees Fahr. 1½ hours, furnace cooled.

Heat Designation	Yield Point p.s.i.	Tensile Strength p.s.i.	Per Cent Elongation in 2 Inches	Per Cent Reduction of Area
"A"	72,550	98,450	25.0	54.15
	72,750	95,250	27.0	55.60
"B"	73,300	92,280	26.0	50.00
	74,450	92,275	29.0	57.45
"C"	76,400	94,550	27.5	50.00
"D"	64,600	84,750	30.0	56.65
"E"	67,900	91,150	27.5	47.20

The test coupons from which these results were obtained, were cast and heat treated integrally with the castings.

Mr. Armstrong's data showing the effectiveness of double normalizing and tempering, are also of interest. This treatment should be especially useful in imparting high physicals to large castings where coarse cast structure is usually found.

Written Discussion: By A. B. Kinzel, Union Carbide and Carbon Co., New York City.

We are in complete agreement with those who have just discussed this paper that the work is most thorough and that the mode of presentation is admirable. The data shown are in accord with general experience on castings of similar analysis. However, we should like to discuss the author's summary.

This discussion is in no way intended as an adverse criticism, but is merely a summarization of the data from a slightly different point of view.

The author has shown that the desired mechanical properties may be obtained provided the manganese content is above 1 per cent. This is true within limits, and the steels referred to by him and described in the paper by J. H. Critchett presented at the American Foundrymen's Association meeting in June 1933, tend to bear out this conclusion. In Mr. Critchett's paper it is shown that an alloy steel with 0.5 per cent chromium and 0.6 per cent silicon gave maximum physical properties with manganese above 1 per cent. However, it is possible to achieve satisfactory physical properties by proper alloy balance without resorting to 1 per cent manganese; for example, for certain purposes a steel casting analysis calling for 3 per cent chromium and less than 0.50 per cent manganese gives values that are better than those shown by the author, and incidentally we should classify the 3 per cent chromium steel as a low alloy steel. To cite specifically, a steel with 0.36 per cent carbon, 0.41 per cent manganese, 0.23 per cent silicon and 3 per cent chromium in the normalized and tempered condition gave a tensile strength of 118,000 pounds per square inch, a yield point of 94,000 pounds per square inch, an elongation of 23 per cent in 2 inches, and a reduction of area of 51 per cent.

It is unfortunate that Heat No. 4 (the sole heat representing the chromium-manganese-vanadium type of steel, does not correspond to our conception of a suitably balanced analysis. Slightly modifying the analysis, a steel of the same type but of suitably balanced analysis may be cited: 0.3 per cent carbon, 1.30 per cent manganese, 0.50 per cent silicon, 0.65 per cent chromium and 0.09 per cent vanadium; this gave a yield point of 80,000 pounds per square inch, tensile strength of 105,000 pounds per square inch, an elongation of 29 per cent, a 60 per cent reduction of area, and an impact value of 57 foot-pounds. The values obtained on Heat No. 4 are even lower than we would expect from the analysis given. That some other factor is involved is shown by the reduction of area and elongation relationship which is unusual.

The erratic values in impact in the as-cast condition are not unusual. Heats 22, 24 and 25 would be expected to give results of the same order of magnitude, but they do not. This is merely mentioned as a caution against drawing any conclusions from impact values in the as-cast condition.

The author has shown definitely that the nickel-manganese-vanadium steels have good physical properties. However, equally good properties may be obtained with less expensive steels such as chromium-vanadium or manganese-vanadium if the analysis is properly selected to give a balanced alloy content.

T. H. NELSON:[3] If there is no further comment I would like to add just a word that is somewhat along the line of the remarks made by Mr. Kinzel; I will still keep down on the lower alloy content and not go as high as 3 per cent. I do not quite altogether agree with Mr. Armstrong's contention that copper is the only alloy that can be safely added without in any way adversely affecting the ductility. I think the straight-carbon molybdenum steels are worthy of a little fuller investigation before that statement is allowed to go by without qualification.

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[3]Midvale Steel Co., Philadelphia.

Author's Closure

Mr. Lorig has submitted an excellent criticism, and though it is not my intention to enter into an involved discussion of the iron-copper system, it is rather difficult to accept the theory that the preferred oxidation of iron to copper causes copper color in steel if the copper is in solution. The fact remains that our experience in making copper-bearing steels has been that castings of simple design do crack as the copper passes some point above 1.00 per cent, providing there is not an appreciable quantity of some alloy to retain the copper in solution, and also, copper as either copper or a high copper-iron alloy can be detected in high copper steels under the microscope (see photomicrographs accompanying this discussion). Inadvertently, the term "segregation" was used to apply to copper not in solution. Mr. Lorig cites the difference in the specific gravity of copper and of iron to illustrate that copper, in the event of segregation, would all settle to the bottom of the casting. There was no suggestion in the paper that the two metals are not completely soluble in liquid solution. Assuming that iron and copper were not even slightly soluble in the solid state it is doubtful that the copper would all segregate to the bottom of castings because of the difference in freezing points of the two metals. In evidence, attention is called to some of the high tin alloys.

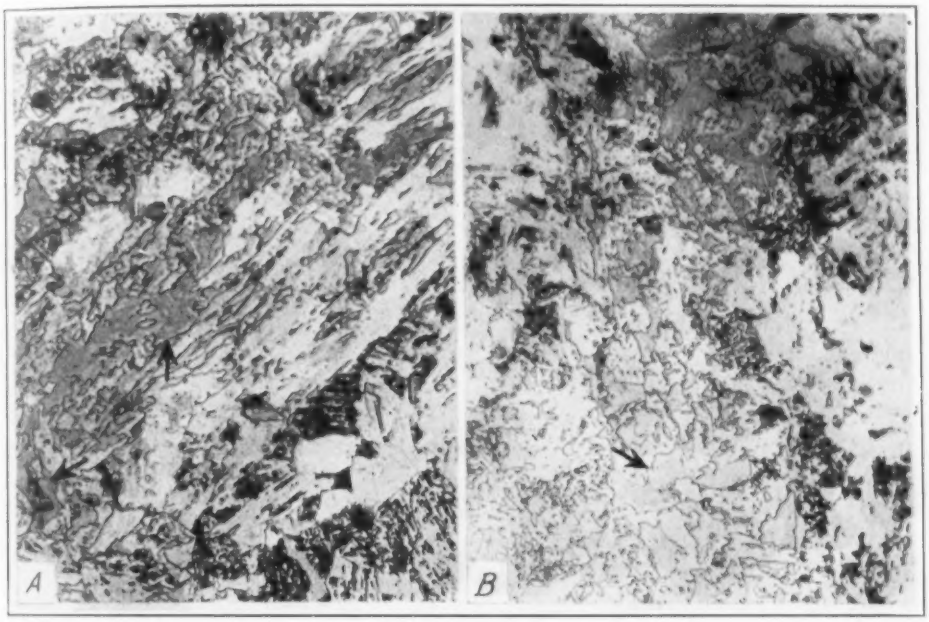

Fig. A—Cast Steel— 0.28 Per Cent Carbon, 1.20 Per Cent Copper, 0.25 Per Cent Nickel. Gray Areas Copper-Rich Constituent. × 500.
Fig. B—Cast Steel—0.31 Per Cent Carbon, 1.14 Per Cent Copper, 0.29 Per Cent Molybdenum. Gray Areas Copper-rich Constituent. × 500.

In answer to both Mr. Lorig and Mr. Finlayson, it was believed not pertinent to discuss the precipitation hardening characteristics of copper steel because discussion in the paper was limited to results obtained on testing and to certain to crack in the mold.

Mr. Zima's opinion that cracks are less likely to occur in nickel-manganese steels if the manganese is held below 1.30 per cent, is concurred in.

Mr. Kinzel has pointed out that it is possible to obtain satisfactory physical properties without resorting to 1.00 per cent manganese if the other alloys are properly balanced, and gives as an example a 3.00 per cent chromium, 0.50 per cent manganese steel. This brings up the question of whether 3.00 per cent chromium would be considered a low or an intermediate alloy steel. Certainly the chromium plus manganese content is higher than the alloy content of most of the steels listed in Table I of the paper. It is also questionable that the 3.00 per cent chromium steel would possess the desired ductility. In the text of the paper it is admitted that the composition of the Heat No. 4 is not properly balanced, but the values obtained from the analysis of a steel containing the same alloys, referred to by Mr. Kinzel, appear to be exceedingly high (29.0 per cent elongation, 105,000 pounds per square inch tensile) for a cast steel that has been either annealed or normalized and tempered.

Mr. Nelson states that the carbon-molybdenum steels should be subjected to more thorough investigation before it is ultimately decided that molybdenum does affect the ductility adversely. In the work published by Gregg[4] are data showing that ductility decreases gradually with increase in molybdenum. Our experience with molybdenum has lead us to the same conclusion.

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[4]J. L. Gregg, "Alloys of Iron and Molybdenum," McGraw Hill Book Co., New York City, p. 115.